A NEW METHOD FOR EVALUATING ACTIVITIES IN TERNARY NONAQUEOUS SOLUTIONS THROUGH INFRARED SPECTROSCOPY

By

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CHAPTER I

INTRODUCTION

Purpose and Scope of the Investigation

It is well known that the thermodynamic activity of each component in a binary solution can be determined rather simply by a number of methods. In general, the activity of one of the components is measured directly and the other is calculated by means of the Gibbs - Duhem Equation (29).

For the direct measurement of the solute activity at a given temperature the e.m.f. method is most commonly used. This method, however, is severely limited in its applicability by the fact that only those systems for which stable reversible electrodes are available can be investigated by this technique.

The alternative to measuring the solute activity directly is, of course, to measure the solvent activity. The more common techniques available for this purpose are the osmotic pressure method (49), the vapor pressure method (5,50) and the isopiestic method (57). Cryoscopic and ebulliometric techniques (30) are also employed for this purpose, but much less frequently because additional information is needed to relate the activity, determined at the boiling or freezing point of the solution, to the activity at some standard temperature, e.g. 25°.

Theoretically at least, the osmotic pressure method is capable of extremely high accuracy, since an ideal 1 molal solution will exert an osmotic pressure of 22.4 atmospheres. However, in practice it is accompanied by such experimental difficulties as to make its use very limited. The isopiestic method, which is actually a vapor pressure method, is quite generally useful in that it can be employed for virtually any binary solution provided that one, and only one, component is volatile. This method has been refined to a high degree by Robinson and co-workers and their data on binary solutions is often considered the standard in the field of electrolyte solution thermodynamics (58). Although the isopiestic method is perfectly applicable to binary nonaqueous solutions, it has not been employed with such solutions to any great extent. One of the severe limitations of this method is the fact that its use requires a very accurate knowledge of the vapor pressure of a reference solution as a function of concentration.

The vapor pressure method has also been employed quite successfully using two other techniques. One, the gas transpiration technique (50), is exceedingly accurate and has been used with excellent success in this laboratory for several years (4,43). It can be used successfully in multicomponent systems, either aqueous or nonaqueous, provided that at least (n-1) of the n components are reasonably volatile and that a method is readily available for analysis of the vapor phase. The ternary systems investigated in this laboratory have been restricted to salts in $HCl-H_2O$ mixtures, at least partly because of the difficulty associated with accurately analyzing a more complicated vapor phase. The static vapor pressure technique (5) is much simpler than the gas transpiration method and would be very much more rapid if only the solution phase could be reliably degassed in a short time. Indeed, one of the most serious objections to the static method is the difficulty in reliably removing all dissolved gases in a reasonable length of time. Since the static method determines the total vapor pressure only, an associated method for analyzing the vapor phase is still required with multicomponent vapors.

The purpose of this research was to develop a method for the determination of activities based upon an infrared spectrum analysis of the equilibrium vapor phase in multicomponent nonaqueous systems. The method should have an accuracy comparable to that of the gas transpiration technique and should be at least as rapid.

The Gibbs-Duhem Equation for Multicomponent Systems

At this point a brief mention of the information necessary to describe the activity of the various components in a multicomponent system seems necessary. The Gibbs-Duhem equation for a multicomponent system is the form,

$$n_1 d\overline{F}_1 + n_2 d\overline{F}_2 \text{ ----- } + n_i d\overline{F}_i = 0 \tag{1}$$

where n_1, n_2 ---- n_i are the number of moles of components 1, 2,.... i respectively, and $\overline{F}_1$, $\overline{F}_2$ .... $\overline{F}_i$ are the corresponding chemical potentials.

By definition,

$$\overline{F}_i = \overline{F}_i^o + RT \ln a_i \tag{2}$$

After substitution of (2) into (1) and simplifying one obtains,

$$n_1 d\ln a_1 + n_2 d\ln a_2 + \ldots\ldots n_i d\ln a_i = 0 \tag{3}$$

Thus it is seen that if the composition of the system and all the activities but one are known, then the unknown activity can be calculated from the above equation. To obtain values for $\underline{a}_i$ Equation (3) must, of course, be integrated. Methods are readily available for obtaining the experimental information necessary for evaluating the resulting integrals when $i = 2$. The solution of Equation (3) for a three component system is vastly more difficult than for the binary, and when $i = 4$ the solution of Equation (3) is impractical.

Attention will therefore be restricted to three component systems. For such a system Equation (3) becomes,

$$n_1 d\ln a_1 + n_2 d\ln a_2 + n_3 d\ln a_3 = 0 \tag{4}$$

and since for ideal gases or vapors $a = p/p^o$ Equation (4) reduces to,

$$n_1 d\ln p_1 + n_2 d\ln p_2 + n_3 d\ln a_3 = 0 \tag{5}$$

or using common logs instead of natural logs

$$n_1 d\log p_1 + n_2 d\log p_2 + n_3 d\log a_3 = 0 \tag{6}$$

dividing (6) by n_1 gives

$$d\log p_1 + n_2/n_1 \; d\log p_2 + n_3/n_1 \; d\log a_3 = 0 \tag{7}$$

If the ratio n_2/n_1 is kept constant, then $n_2/n_1 = k$.

Using this relation and transposing, Equation (7) becomes,

$$d\log p_1 + k \; d\log p_2 = - n_3/n_1 \; d\log a_3 \tag{8}$$

Integration of (8) gives,

$$\int n_1/n_3 \; d\log p_1 + k \int n_1/n_3 \; d\log p_2 = - \int d\log a_3 \tag{9}$$

Since $n_1/n_3 = \dfrac{\dfrac{1000}{M_1}}{m_3} = \dfrac{K}{m_3}$, where

M_1 = molecular weight of component 1

m_3 = molality of component 3

Equation (9) becomes

$$K \int d\log p_1 / m_3 + Kk \int d\log p_2/m_3 = - \log a_3 + C \tag{10}$$

Thus if log p_1 and log p_2 can be expressed as some analytical function of $\underline{m}_3$, such as a simple power series, the integration of the left hand side of the equation is easily performed analytically. To evaluate the constant C one must know $\underline{a}_3$ in some reference state, e.g., the saturated solution. If the solid phase in both the binary and ternary solutions is the same, one can readily relate the activity of the salt in the saturated ternary solution to the activity of the salt in the saturated binary solution as described in a later section.

In order to achieve the objective of this research it was necessary to devise a method for accurately and rapidly evaluating the partial pressures of volatile components 1 and 2 from infrared data.

The Infrared Approach

It was recognized that if the method was to be quite generally useful, it should be applicable to systems in which components 1 and 2 were any of a wide variety of volatile organic compounds.

It is well known that all organic compounds absorb radiation in the infrared region of the electromagnetic spectrum. It is also well known that no two compounds have identical absorption spectra in this region. Thus, it should be possible to detect component 1 in the presence of component 2, and if certain requirements are met regarding the position and intensity of the absorption bands, it should also be possible to determine the concentrations of components 1 and 2 in mixtures with each other. It was for this reason primarily that the infrared spectrophotometric technique was chosen to attack the problem.

Consider the case of a ternary solution consisting of two volatile organic components and an involatile solute. If the ratio of n_2/n_1 is kept constant as required by Equation (8) and n_3 is varied over a wide range of concentrations, then the equilibrium vapor pressure exerted by each of the volatile components will vary in some regular fashion as the concentration of component 3 is changed. At all values of n_3, the partial pressures p_1 and p_2 are related by Dalton's Law.

$$P_t = p_1 + p_2 \tag{11}$$

Here P_t is the total pressure exerted by the system. If P_t is accurately measured at equilibrium and if either p_1, p_2 or the ratio of p_1/p_2 is also determined, then both partial pressures can be found.

Liquid and Vapor Phase Methods

At least two methods of utilizing infrared spectroscopy as a means of determining p_1 and p_2 immediately suggested themselves. The vapors in equilibrium with any given ternary solution could be introduced into an infrared gas cell and analyzed directly in the vapor phase, or the equilibrium vapors could be quantitatively condensed, dissolved in a suitable solvent and analyzed in the liquid phase. Both of these approaches were tried during the course of this research. The former method was not very successful and was abandoned after considerable work was done on it. The latter method was found to be quite satisfactory but only after it was decided to use the near infrared region of the spectrum for analysis.

Although the first approach, i.e., the vapor phase analysis did not prove entirely successful, nevertheless, a brief mention will be made of it at this point so that one can appreciate the reason why this approach was chosen first. It appeared that the most obvious and apparently the simplest technique would be to construct an apparatus to measure $\underline{P}_t$ at equilibrium, by means of the static method, and then to allow the equilibrium vapors to expand into an evacuated infrared gas cell of fixed dimensions and obtain $\underline{p}_1$ and $\underline{p}_2$ by the use of Beer's law. Beer's law can be expressed as

$$\text{O. D.} = K c_i \tag{12}$$

where O. D. is the optical density or absorbance of the vapors. Since pressure is also a concentration term one may write (12) as

$$\text{O. D.} = k p_i \tag{13}$$

If two wave lengths, $\lambda = A$ and $\lambda = B$ are chosen such that component 1 absorbs strongly at A and weakly at B, and component 2 absorbs strongly at B and weakly at A, and if Beer's law is followed for both components at both wave lengths, then the optical density at A and B is given by:

$$(\text{O. D.})_A = k_1 p_1 + k_2 p_2 \tag{14}$$

$$(\text{O. D.})_B = k_3 p_1 + k_4 p_2 \tag{15}$$

where

k_1 = absorption coefficient of component 1 at wave length A
k_2 = absorption coefficient of component 2 at wave length A
k_3 = absorption coefficient of component 1 at wave length B
k_4 = absorption coefficient of component 2 at wave length B
$(\text{O. D.})_A$ and $(\text{O. D.})_B$ = optical density or absorbance at wave length A and B respectively.

The $\underline{k}$ values can be calculated by determining the optical density of both pure components under known pressures at the wave lengths A and B and solving Equation (13) for $\underline{k}_1$, $\underline{k}_2$, $\underline{k}_3$, and $\underline{k}_4$. Having thus determined the $\underline{k}$ values, one can solve (14) and (15) simultaneously for the unknown quantities $\underline{p}_1$ and $\underline{p}_2$.

For a number of reasons which will be discussed later, Equation (13) did not correctly express the relationships between O. D. and p_i for the compounds investigated, and consequently Equations (14) and (15) were only useful as first approximations. Aside from this theoretical difficulty, the vapor phase technique presented serious experimental difficulties which will also be discussed later.

In the liquid phase method, the equilibrium vapors are quantitatively condensed, dissolved in a transparent solvent, and the concentration of each component calculated from Equations (16) and (17) which are analogous to (14) and (15)

$$(\text{O. D.})_A = k_1c_1 + k_2c_2 \qquad (16)$$

$$(\text{O. D.})_B = k_3c_1 + k_4c_2 \qquad (17)$$

Here c_1 and c_2 are the concentrations of components 1 and 2 in grams / 100 grams of solvent. Equations (16) and (17) can be solved simutaneously to yield the ratio (c_1/c_2). From the values of this ratio the partial pressures p_1 and p_2 can be calculated from the following equations:

$$p_1 = \frac{P_t}{1 + \frac{M_1}{M_1}\frac{c_2}{c_1}} \qquad (18)$$

$$p_2 = \frac{P_t}{1 + \frac{M_2}{M_1}\frac{c_1}{c_2}} \qquad (19)$$

where P_t = the total equilibrium pressure, M_1 and M_2 = the molecular weight of components 1 and 2 respectively. Since the liquid phase technique proved highly successful, it will be described in detail in a later section.

Literature Survey

A survey of the literature indicated that very few studies had been made in which the activities of all of the components in multicomponent systems were determined. In addition to the work done in this laboratory on solutions of transition metal salts in $HCl-H_2O$ mixtures, considerable work has also been done on systems in which all three of the components were volatile (31, 33, 34, 47, 53). However, with such systems it is not necessary to use the Gibbs - Duhem equation to calculate activities, because they can be computed directly from the relation,

$$a_i = \frac{p_i}{p_i^o} \tag{20}$$

Some work has been done on ternary systems containing one organic component such as alcohol, a salt and water (37). In such instances, however, the activity of the salt was not calculated. The electromotive force method has been employed to some extent to determine the activity of HCl in water - alcohol mixtures (6, 25, 42, 44, 48). In these experiments, however, the activity of the organic component was not determined.

No work at all has been reported on the determination of the activities of all components in ternary nonaqueous solutions containing an inorganic salt. In fact, it is very surprising to note an almost complete lack of information available on the activities of even binary nonaqueous solutions containing an inorganic salt, despite the fact that such information is rather easy to obtain and could be of considerable importance in elucidating the thermodynamics involved in distillation or liquid-liquid extraction experiments. For a few systems of special interest, however, some data are available. For example, Rowley (60) has measured the vapor pressure of diethyl ether solutions of magnesium bromide. In this instance, however, the activity of the salt was not calculated.

Infrared spectroscopy has long been used for the quantitative identification of organic compounds (7), and more recently it has been used for the different components in mixtures. The literature contains many reports on the quantitative analysis of many different compounds, both alone and in mixtures with other compounds. The journal, Analytical Chemistry, now devotes a special small section to infrared quantitative analysis data. The number of papers published on the analysis of various organic compounds by different infrared techniques is too great to list; however, certain selected references from the general literature will be given to provide the necessary background information concerning the theory and techniques of infrared spectroscopy in general. A few references will also be given to papers concerned with the quantitative analysis of compounds containing functional groups, the same as, or simular to the ones investigated in this research.

Karcher (26) has described an apparatus and procedure for the accurate determination of the concentration of ethanol in either liquid or gaseous hydrocarbon streams. Colon and Frediani (8) have determined the concentration of alcohol in ether by an infrared technique. Heacock (18) has informed the author that the infrared spectroscopy group at the Phillips Petroleum Company Laboratories often performs routine analyses accurate to 1% on six-component hydrocarbon systems. Hudson (23) has recently reported on the accurate analysis of a ten-component halogenated hydrocarbon system.

Analysis of hydrocarbons is, in general, simpler than that for polar compounds because hydrocarbons form more nearly ideal solutions, and their absorption maxima do not shift very much with concentration or temperature. There are many other factors which make hydrocarbon systems easier to work with, but it is unnecessary to list them here. Liquid hydrocarbons were not considered in this work because of the extremely low solubility of inorganic salts in them.

Friedel (13) has very recently published a critical summary of the uses and limitations of analytical methods involving infrared spectra in the vapor state.

Since it was only quite recently that spectrophotometers utilizing detectors sensitive to radiation in the near-infrared region have become commercially available, it is understandable that the number of analytical investigations in the near-infrared or overtone region is quite small. Few quantitative analyses in this region have been carried out, even though the relative simplicity of the spectra and the excellent electronic and optical properties of the near-infrared spectrophotometers make this region an almost ideal one in which to perform many types of analyses. Some work in the near-infrared has been reported, however.

Mecke (38) has investigated the effect of hydrogen bonding on the OH absorption band in the near infrared.

Mitchell et al. (41) have determined the acetyl content of cellulose acetate by determining the concentration of residual OH groups. This analysis was performed with an error of less than 1% by absorption spectrophotometry in the near infrared region.

Very recently Washburn (68) has determined the concentration of pentanol in bromopentane with an accuracy of better than 1% by utilizing the absorption band at 2740 millimicrons which is characteristic of the

OH group in most alcohols.

While not much literature is yet available on analytical techniques in the near infrared, a wealth of general information on the theory and practice of medium infrared spectroscopy is available. The article by Jones and Sandorfy (69) should be read by anyone seriously considering experimentation in infrared spectroscopy. Bellamy's book (1) on the infrared spectra of complex molecules also contains interesting and informative material for the beginner as well as for those experienced in the field.

Thompson and Sutherland (66) have reviewed the field of infrared spectroscopy and offer many helpful suggestions for the novice.

A paper by Gorden and Powell (15) was found to be extremely helpful in initiating some of the early work of this research. The authors discussed the merits of various experimental procedures and the effect of many variables on the accuracy obtainable by the infrared method. The Perkin-Elmer manual (51) which is furnished to purchasers of Perkin-Elmer instruments should also be consulted by the beginner. Here, many techniques are discussed in very simple language and many references are given to more detailed explanations of certain phases of infrared spectroscopy.

Nielsen (45) Brattain (2) and Friedel (12) describe several methods for determining accurate optical density values from I. R spectra. They also define terms and nomenclature which are accepted as standard by the <u>Journal of Analytical Chemistry</u> in which most of the quantitative infrared data are published.

CHAPTER II

EXPERIMENTAL

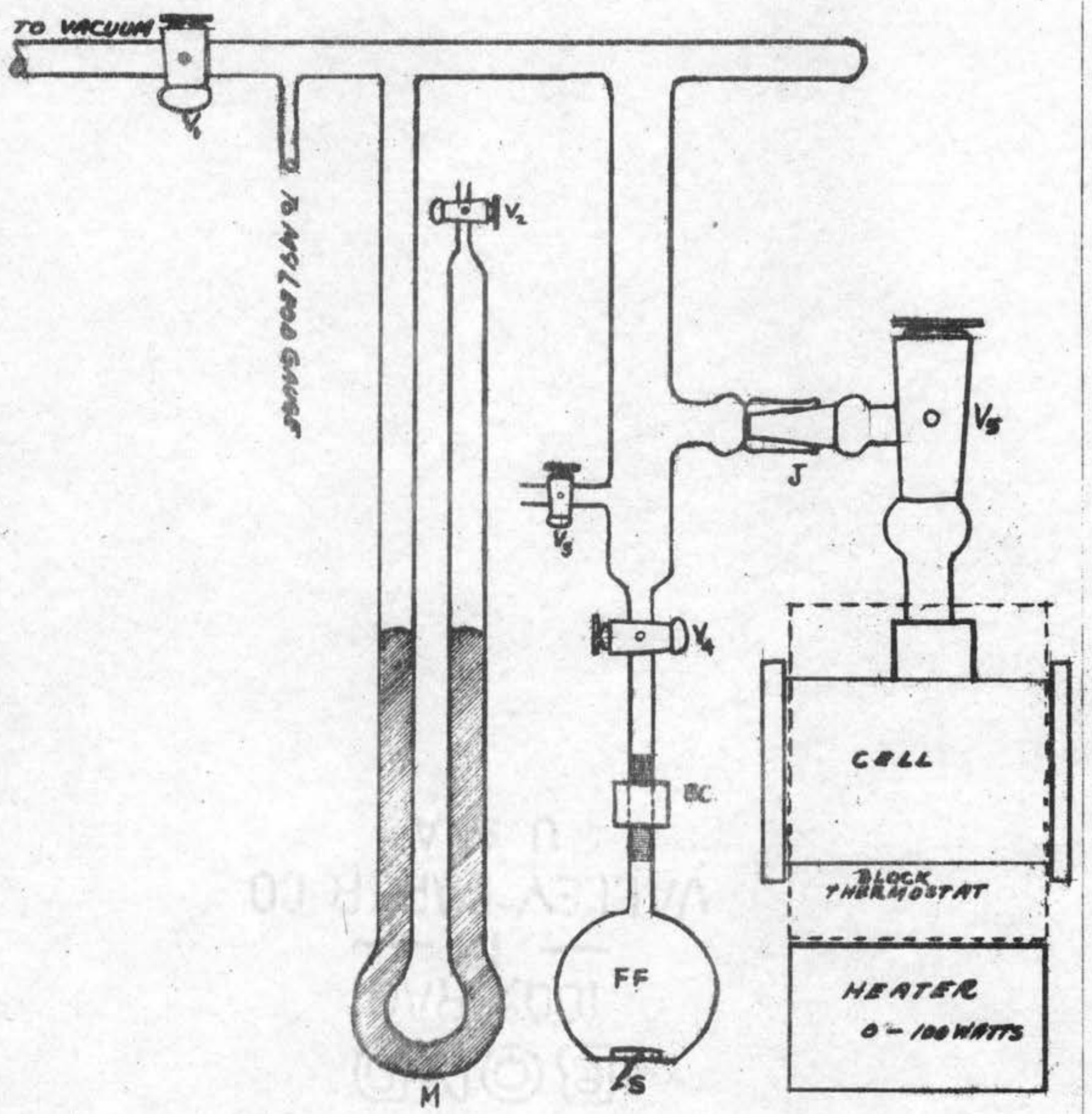
Apparatus

The First Gas-Phase Apparatus.

As mentioned earlier, the first method of approach to the problem of measuring the partial pressure of the various components in the equilibrium vapor phase was a direct vapor-phase analysis. Hence it was necessary to design and test an apparatus in which one could collect and analyze various organic vapors at known partial and total pressures. Since changes in design were constantly being made during the course of the research, it is impractical to describe all the experimental modifications. There were, however, essentially two different types of apparatus used in the vapor-phase analysis experiments. Since the vapor-phase technique proved unsatisfactory for precise quantitative measurements, the apparatus used in these experiments will be only very briefly described.

In general, the apparatus shown in Figure 1 was manipulated as follows: The organic liquid to be tested was first thoroughly degassed by distilling under vacuum several milliliters of liquid from flask $\underline{F}$ through the valve $\underline{V}_1$ into a cold trap placed before the vacuum pump. After about 10 ml. of liquid had been distilled, all of the dissolved gases were considered removed. The entire system (with the exception of $\underline{F}$) was then evacuated until the pressure was 0.02 mm as read by the

FIGURE #1   1st VAPOR PHASE APPARATUS



McLeod Gauge. Then with $\underline{V}_1$ closed, the organic vapor was admitted into the system until the desired pressure was obtained, the pressure in the system being read on manometer $\underline{M}$. Cell $\underline{C}$ was removed, and the optical density of the gas was determined by infrared absorption. Since it was later found necessary to measure optical densities at the same total pressure regardless of the partial pressure of the organic vapor, nitrogen, which is optically transparent, was introduced into the system through $\underline{V}_5$ in order to bring the pressure in the cell to a predetermined value, e.g. 122 mm Hg.

High Vacuum Valves.

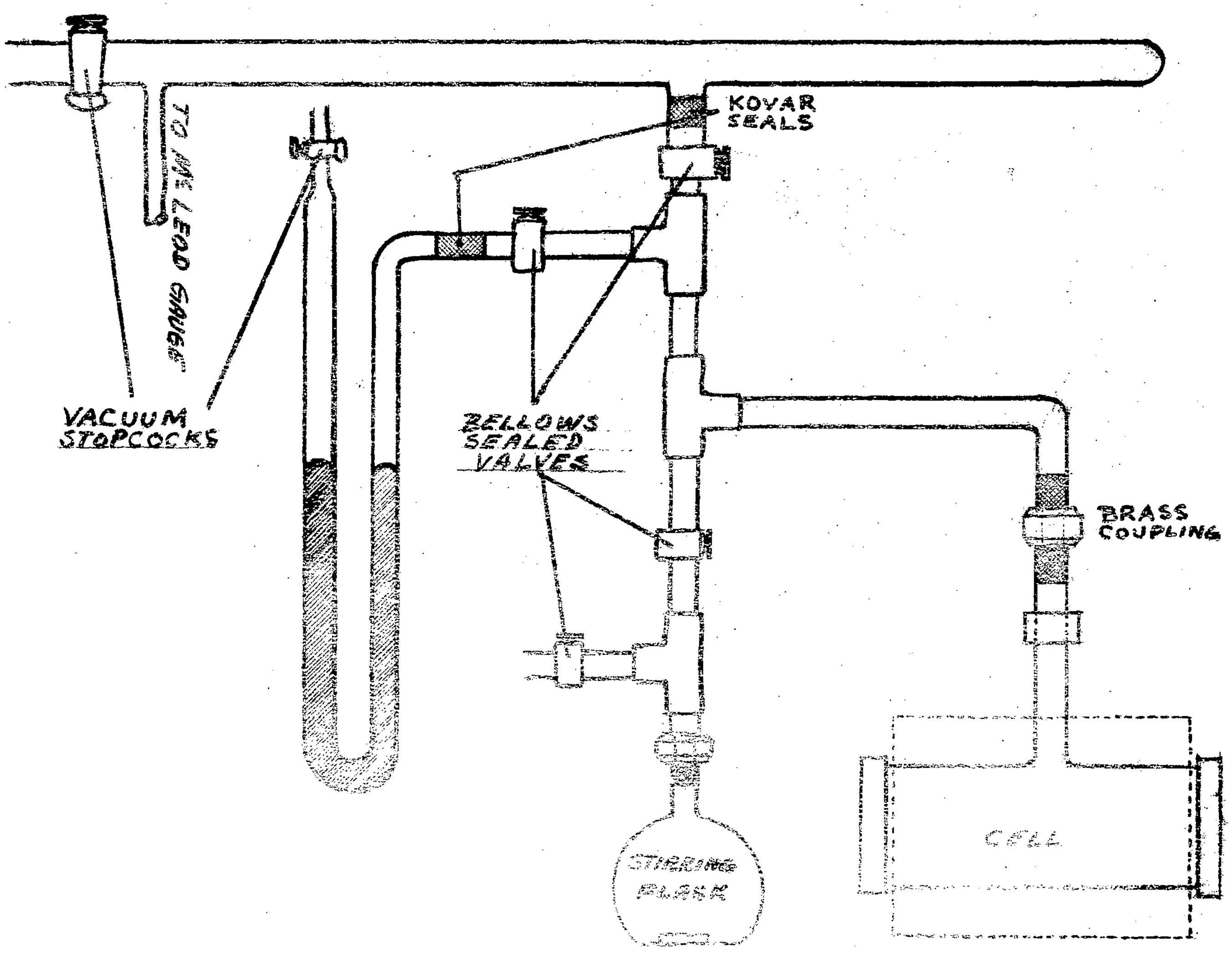
Early work showed that the system employing lubricated stopcocks was entirely unsatisfactory because of adsorption of the vapors by the stopcock $\underline{V}_2$ since it was constantly in contact with the vapors. It was found necessary also to dismantle the large stopcock $\underline{V}_2$, clean it, regrease it, and reassemble it whenever a new vapor was introduced into the cell.

To avoid the difficulties associated with stopcocks it became necessary to modify the apparatus by introducing bellows-sealed high vacuum valves in place of vacuum stopcocks. At the time Hoke, Inc. (21) manufactured the only valves suitable for this purpose (Model 434). They were brass needle valves similar to those used to regulate the flow of compressed gases e.g. O_2, N_2, H_2, etc., with, however, a bronze bellows instead of packing to provide a more positive seal against leakage and contamination.

Second Gas Phase Apparatus.

The gas-phase apparatus (Figure 2) was quite similar in design to

FIG #2 2nd VAPOR PHASE APPARATUS



the original, with the exception that the needle valves described above were used in place of the vacuum stopcocks. The apparatus was constructed mainly of 3/8" copper tubing instead of glass. This resulted in a stronger and more flexible system than the previous all-glass one. The method of operation was precisely the same except that the cell was removed for analysis by unscrewing the brass coupling $\underline{BC}_1$ connected to the valve $\underline{V}_3$ instead of by disconnecting the standard taper joint as with the previous design (Figure 1).

Although the new design eliminated a very serious difficulty, that of adsorption of the vapors by the lubricant, it introduced a few new difficulties of its own. The most serious disadvantage introduced by the use of metal high-vaccum valves was the greater possibility of leakage. This was complicated by the impossibility of using a Tesla coil to locate the leaks when they did occur. Associated with each valve, there were a total of four likely locations where leakage could occur: the two couplings which joined the valve to the rest of the system, the seat, and the bellows. The danger of leakage was very real too, since leaks were discovered at each of the locations described above at various times during the operation of the apparatus.

Besides the possibility of leakage at the valves there existed the even more serious danger of leakage at the windows of the gas cell. The gasket material used to make a high vacuum seal between the cell and the silver chloride windows had to be of such a nature that it would not preferentially adsorb any vapor with which it came in contact. This eliminated natural rubber, neoprene, apiezon wax, polyethylene, etc. Teflon and amalgamated lead were used but without any real success. Teflon, unfortunately, was found to have the property of "Creeping" under pressure and would not hold a vacuum for any great length of time. The amalgamated lead gaskets reacted with the silver chloride windows and liberated crystals of free silver, thereby ruining the windows and allowing leakage. When no gaskets were used at all the brass cell reacted with the silver chloride windows. Possible methods of eliminating some of these difficulties are discussed in a later section.

The Condensed Phase Apparatus.

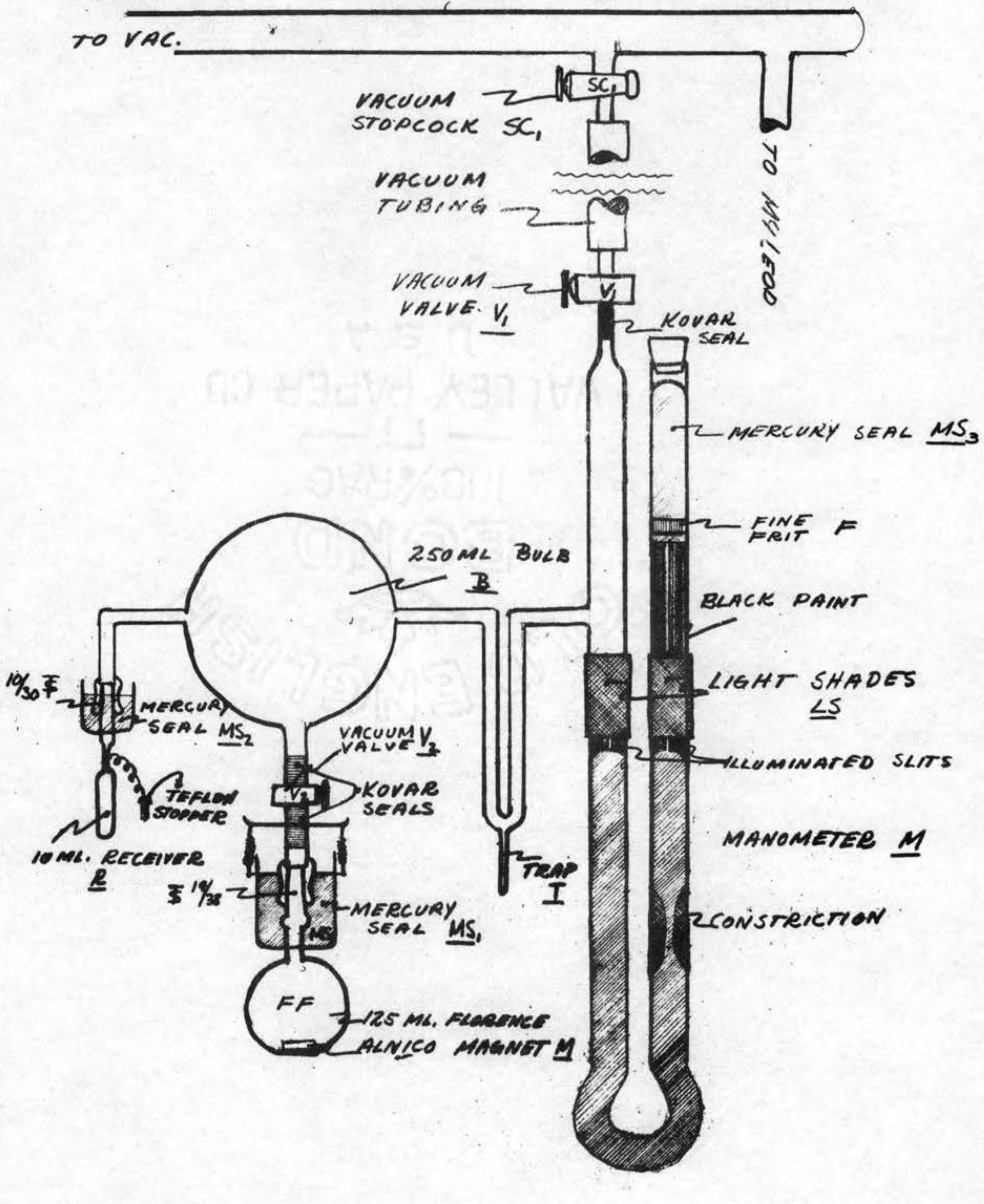
When it was determined that Beer's law was indeed followed quite closely by the compounds under investigation at wavelengths in the near infrared, it was decided to construct an apparatus which would permit one to measure P_t and then to quantitatively condense the equilibrium vapor. It should be as simple and accurate as possible, yet rugged enough to stand long use without failure. The final design of this apparatus satisfactorily met these requirements. It was exceedingly compact, employed only two valves, and was extremely rugged. It was used for about six months without failure of any of its parts.

Since this apparatus proved so highly successful, it will be described in some detail and a short explanation will be given of the function of the various parts.

The condensed-phase apparatus is shown in Figure 3. The components not shown are the Welch Duo-Seal pump, capable of a vacuum of better than 10 microns of mercury, and a tipping McLeod gauge with a range from 1.0 micron to 1.0 mm of mercury pressure.

The glass stopcock SC_1 which was a permanent part of the vacuum system was a special high-vacuum type fabricated by Corning. Dow silicone high-vacuum stopcock grease was used as the lubricant. The rubber tubing was a four-foot length of flexible heavy-wall vacuum

FIGURE #3 — CONDENSED PHASE APPARATUS



tubing which allowed movement of the entire apparatus from the bench to the constant temperature bath. Both $\underline{V}_1$ and $\underline{V}_2$ were vacuum valves of a new type manufactured by Hoke, Inc. (A 434) which were free from some of the disadvantages of the earlier models (see the above section on the gas-phase apparatus). Valves $\underline{V}_1$ and $\underline{V}_2$ were joined to the glass system <u>via</u> 3/8" O. D. Pyrex to Kovar graded seals purchased from Wakefield Industries (67). The manometer was constructed from 16 mm heavy-wall Pyrex tubing. A narrow constriction of about 1 mm was put in one arm of the manometer to prevent the mercury from rupturing the closed end in the event that gas was introduced too rapidly into the system. On to the "closed end" of the manometer there was sealed a fine Pyrex frit. After evacuation of the manometer thru the frit, it was closed by a column of clean mercury about 40 mm in height. This was used rather than a glass seal because it greatly facilitated cleaning the manometer, and also enabled one to easily pump out any air that had desorbed from the walls of the manometer. The entire back of the manometer was painted with blackboard paint except for a vertical slit about 1 mm wide down the center of the tubing which was left unpainted. Light shields were made from thin aluminum foil in such a fashion that they could slide up and down each arm of the manometer. Before each reading these were placed about 1 mm above the mercury meniscus to prevent any stray light from striking the mercury surface; the vertical slit was illuminated from behind and the height of the menisci were read with a Gaertner cathetometer to the nearest 0.1 mm. With the above precautions the meniscus appeared as an extremely sharp line and could be easily and accurately read. If such precautions were not used, reflections from the mercury surface made it impossible to determine the exact position of the meniscus, and reproducible readings could not be made.

Connecting the manometer to the bulb was a U-shaped mercury trap. This was considerably more flexible than a straight piece of tubing, and it effectively prevented mercury from entering the bulb, dripping down in $\underline{V}_2$ and ruining it by amalgamation. Occasionally a few small droplets of liquid condensed in the left arm, and when the system was evacuated the liquid boiled violently and pushed mercury out of the manometer into the trap. At intervals the bottom was removed from the trap, the mercury discarded and a new bottom put in.

The solution to be examined was placed in the 125 ml Florence flask FF equipped with a small uncoated alnico bar magnet. Glass coated magnets were found to be unsatisfactory because they invariably broke and released air into the previously degassed system. Teflon covered magnets were regarded as unsuitable because they have been known to explode under vacuum. Plastic coated magnets could not be used because they reacted with the solution. Alnico itself, however, was completely inert toward the system used and would be expected to be inert towards most organic compounds. The flask was equipped with a ₸ 19/38 male joint which was specially lapped into the female joint sealed to the rest of the system. The finest grade (600 mesh) of carborundum was used for the preliminary grinding and Fisher polishing alumina was used for the final polishing. This resulted in an extremely close fit which had very little tendency to bind and was practically vacuum tight even without the mercury seal. When joints were used as they came from the manufacturer, they tended to bind, and it became very difficult to detach FF from the system.

The receivers *R*, made from a 28 mm test tube and a ₮ 10/30 male joint, were designed to hold 10 ml of liquid. Since they were to be subjected to very low temperatures, they had to be annealed carefully before use. The ₮ 10/30 joint of each received was specially lapped as described, and in addition was sealed with mercury. After collection of a sample, the receiver was closed by a specially fabricated teflon stopper. Individual stoppers were made for each receiver because the fit was so exact that they could not be interchanged. As an example of their effectiveness, a receiver containing CS_2 was sealed with a teflon stopper and weighed to the nearest 0.1 mg.; three days later it was weighed again and showed no loss in weight. The stoppers were made as follows: A 1/4" teflon rod was rotated in the chuck of a drill press until it had an extremely gentle taper. It was then just able to fit into the receiver neck. The stopper, while still rotating was then gently forced into the neck of the receiver. Under the influence of the gentle pressure and the heat generated by friction, the teflon "flowed" very slightly and assumed the exact dimensions of the receiver neck. The stopper also acquired a glass-like smoothness as a result of this treatment.

Cells.

Infrared Gas Cell. The two infrared gas cells (Figure 4) were each fashioned out of brass and were fitted with silver chloride windows of about 5 mm thickness. Thinner and consequently more transparent windows were tried but were found to be completely unsatisfactory. When subjected to a vacuum for even a short time, the thin windows became deformed, thereby losing their planarity and changing the effective path cell. The silver chloride windows were made by Harshaw Scientific Company (7).

FIG # 4a
VAPOR CELL

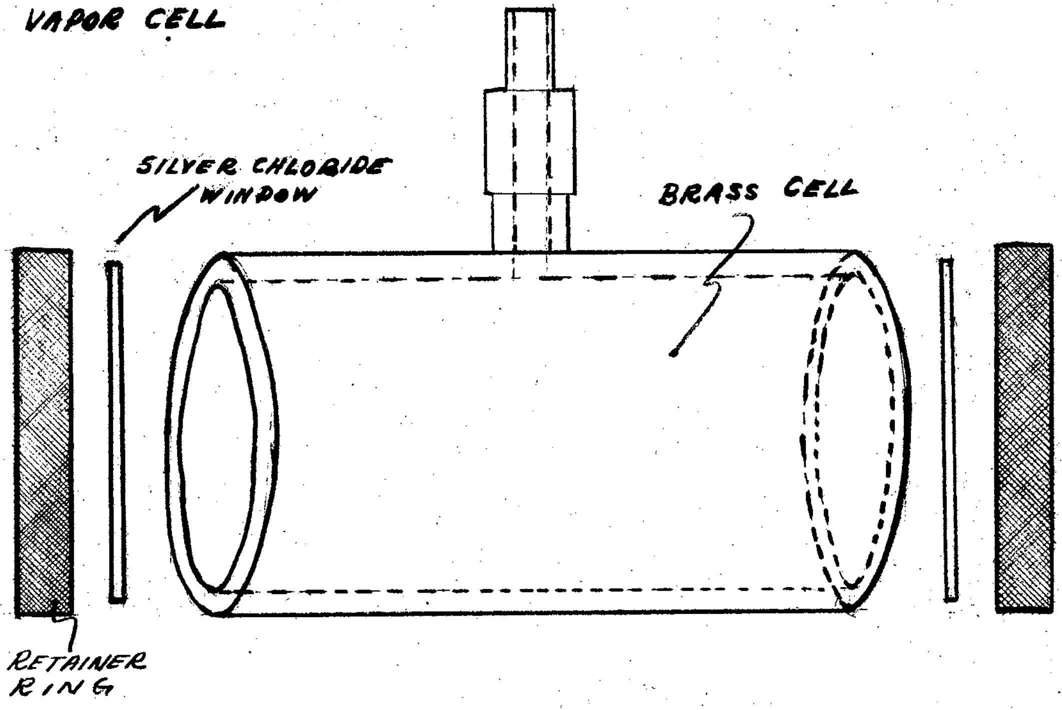
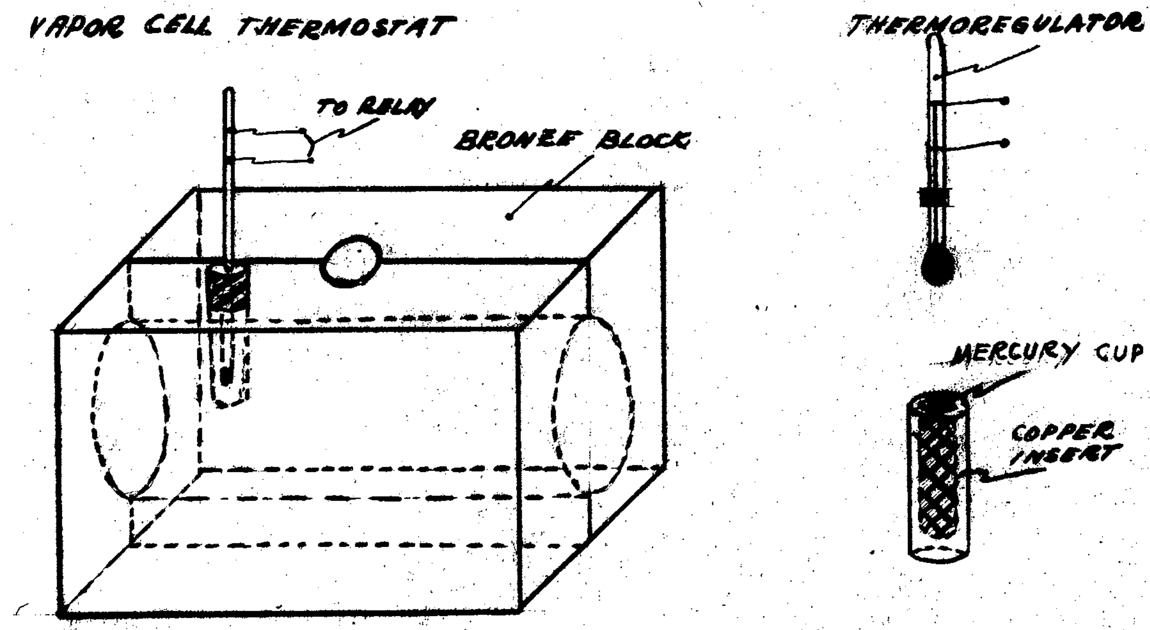


FIG # 4b
VAPOR CELL THERMOSTAT



Medium Infrared Liquid Cell. The cell used for liquid-phase analysis in the medium infrared was a standard fixed-thickness cell manufactured by the Perkin-Elmer Corporation. The thickness was 1.0 mm and the windows were of rock salt. The cell was filled by means of a hypodermic syringe and sealed with teflon stoppers provided by the manufacturer.

Near Infrared Liquid Cell. The cells used for analysis in the near infrared were standard 10 mm matched silica cells manufactured by Pyrocell Company (56). No commercially available liquid cell was found suitable for use with such highly volatile solvents as CS_2, CCl_4, so the standard cells were modified as follows. A 6 mm diameter hole was drilled in a piece of glass 13 mm x 13 mm x 5 mm. This hole was tapered slightly by grinding with carborundum and a tapered carbon rod. The final grinding was done with a ₸ 7/25 male joint and polishing alumina. The male joint was sealed with a torch at the top and bottom and this was used as the stopper for the cell. The flat piece of glass was sealed to the silica cell with "water glass." It could be removed for cleaning the cell by immersing it in hot water for about an hour. This type of cell proved to be completely satisfactory.

Thermostats.

The Gas Cell Thermostat. The gas cell was thermostatted during the filling process by mounting it in an 8 pound bronze block fitted with a thermometer well (Figure 4b). Into the thermometer well was placed a drilled copper rod filled with mercury. A thermometer type thermoregulator (37°) placed in the mercury filled tube actuated a 100 watt hot-plate *via* a Cenco-Gilson electronic relay. The hot-plat rheostat was adjusted so as to operate at about 20 watts. Temperature control was accurate to about 0.1°.

Thermostat for Condensed Phase Apparatus. The thermostat for the condensed-phase apparatus consisted of a large (9 gallon) cylindrical Pyrex jar filled with water. Heat was supplied by a 100 watt knife-type heater actuated by a mercurial thermoregulator *via* a Fisher-Serfass electronic relay. Cooling was by cold water (about 15°) passed at a slow rate thru 12 feet of coiled 3/8" copper tubing. Extremely efficient stirring was obtained by use of a Little Giant centrifugal pump submersed in the bath (32). The temperature was kept at 25.00° ± 0.01° and was measured by a thermometer (Cenco #19247) graduated in 0.05° divisions, which had been calibrated in the laboratories of the Continental Oil Company, Ponca City, Oklahoma against a 0.01° thermometer calibrated by the National Bureau of Standards, Washington, D. C.

Spectrophotometers.

The Perkin-Elmer Model 12C. All of the spectrophotometric measurements made in the medium infrared, i.e. all of the gas-phase measurements and some of the early liquid-phase measurements, were made with the Perkin-Elmer Model 12C single-beam infrared spectrometer. This instrument was equipped throughout with sodium chloride optics. As mentioned earlier the liquid cell also had sodium chloride optics, but the gas cell was equipped with silver chloride windows. The first data were obtained by calculating the optical density from the observed optical transmission values, $\underline{I}$ and $\underline{I}_o$, recorded by an L & N speedomax recorder. Large voltage fluctuations of the electricity in the laboratories caused objectionable drift and instability in the recorder amplifier, and as a result the transmission values varied by ± 1% or more of full scale during the course of an analysis. Later measurements were made by by-passing the recorder completely and recording $\underline{I}_o$ and $\underline{I}$ with a Rubicon "High Precision Type B" potentiometer. Besides eliminating much of the instability and drift it effectively "expanded" the transmission scale so that optical densities could be calculated with much greater degree of accuracy. A very excellent description of the theory and operation of the instrument is available in the Perkin-Elmer Instruction Manual (51).

The Beckman Model DK-1. The final and most successful analyses were made using the near infrared region of the spectrum (3.0 micron - 0.9 micron) and the Beckman DK-1 quartz spectrophotometer. Whenever this region and the medium infrared can both be used for analysis, the DK-1 is to be greatly preferred because it offers many optical, mechanical and electronic advantages over the older 12-C. However, in general, the medium infrared region is much more useful especially for qualitative analysis than the near infrared. No description of the instrument needs to be given except to mention that it is an automatic scanning double-beam spectrometer equipped with quartz optics. Detection of near infrared radiation is accomplished by an extremely sensitive lead sulfide detector. The double beam feature allows exact compensation for solvent and cell absorption and automatically compensates for such variables as fluctuation of source intensity, small variations in line voltage, changes in amplifier characteristics, etc.

Miscellaneous.

Standard Solution Vials. In the preparation of standard solutions of highly volatile compounds, extreme care must be exercised to prevent evaporation during, and after, the preparation of the samples. Standard solutions were prepared in ten 10 ml-vials similar to the receivers described earlier (Page 20) except for not having the male joint. The ends were fire polished and flared slightly with a carbon rod. Individual teflon stoppers were fabricated for each individual vial by the method already described. The standard stock-solution was prepared in a 40 ml vial with the same type neck and stopper.

Stirrer. Stirring of the solution in the condensed-phase apparatus was done by a unique submersible stirrer designed and built by Dr. C. E. Miller of this laboratory.

Procedure

Investigation of Possible Compounds for use in the Vapor Phase.

After construction of the apparatus (Figure 1) attention was given to the selection of organic compounds which might be used in the study. While in principle, virtually any compound could be used for investigative purposes such as these, it seemed desirable to choose initially those compounds whose properties were such as to minimize experimental complications. Ideal compounds should therefore fulfill the following criteria:

1) The compounds should have one or more strong absorption bands which are characteristic of an atomic group peculiar to this compound only.

2) The absorption band should be at a frequency where all other compounds in the system show little or no absorption.

3) The compounds should have appreciable vapor pressures at 25^{o}, e.g. about 40 - 200 mm Hg.

4) All compounds to be used in mixtures should be miscible in all proportions.

5) The compounds should be easy to obtain in a high degree of purity with a minimum of purification techniques.

6) They should show extreme chemical stability at temperatures up to 40° with respect to oxidation, decomposition, etc.

7) They should show solvent properties for inorganic salts.

8) They should not undergo chemical interaction in either the liquid or the vapor phase.

9) The vapors should behave as nearly as possible like ideal gases.

Compounds Tried and Chosen. On the basis of the above criteria, the following compounds were considered possibilities: methanol, ethylene chloride, acetone, ethyl ether, carbon disulfide, carbon terachloride, and chloroform. The first step in determining the suitability of the above compounds was to obtain their individual absorption spectra at various pressures over the entire frequency range suitable for analytical purposes. After this had been done, all of the spectra were compared with one another to determine which compounds were optically incompatible. It was recognized that if the absorption spectra of two compounds were such that the only useful absorption bands strongly interfered, a mixture of such compounds would be extremely difficult to analyze by purely optical methods, and such components must be considered mutually incompatible. Some compounds like ethyl ether were found to be incompatible with all the others because at its normal vapor pressure (537 mm at 25°) the optical density over the entire spectral range was so great that the detection of any other component in a mixture would be impractical.

After considering all of the criteria mentioned earlier, as well as the shape and the intensity of the absorption spectra, it was concluded that of the compounds mentioned earlier, methanol and ethylene chloride would form the most satisfactory mixture.

Vapor Phase Analysis.

Optical Density Measurements of Methanol and Ethylene Chloride. To find the concentration of both components in a mixture from a measurement of the optical density, two methods can be used. The first and simpler method can be used if both substances obey Beer's law at the wave lengths chosen. As shown in an earlier section, this method simply requires the solution of the two simultaneous equations representing Beer's law, Equations (14) and (15). If Beer's law is not followed over the entire range of concentrations, a graphical solution may still be possible. This method of iteration is actually a method of successive approximations and requires only that we have a graphical relationship between the optical density and concentration for both components at both wave lengths. This second method is, at best, quite time consuming but, nevertheless, finds extensive application in industrial process control because quite often in practice, systems of interest deviate considerably from Beer's law.

Regardless of which of the above methods are used, it is necessary to obtain optical density-concentration data over a wide range of concentrations. Hence the logical first step toward the analysis of mixtures in the vapor phase, was to try to obtain the relation which precisely described the optical density of a vapor as a function of its concentration or partial pressure. Since the vapor-phase method was tried first but was eventually abandoned in favor of simpler and more reliable methods, it suffices to mention only briefly the more important techniques and to graphically summarize the data. Only as much detail is given as is considered necessary to clearly describe the essentials of the operation.

Measurement of Optical Density at Variable Total Pressure. In the first set of experiments the brass cell was completely evacuated and either air-free methanol or ethylene chloride was admitted into the system. Since the total pressure P_t in the cell was that produced by the pure organic vapor alone, $P_t = p_i$, where p_i is the partial pressure of the vapor. The pressure P_t was read from the manometer, and the cell was removed for analysis. The cell containing the vapor at known pressure was then placed in the light path and the transmission I was read directly from the recorder. Because the spectrometer would not reproduce the 100% transmission line, I_o, over long periods of time, e.g. ten minutes, it was necessary to use the following scheme for obtaining I_o. This was obtained at any desired wave length by putting the evacuated cell in the light path and setting the recorder at 100% transmission. Then a beam attenuator in the form of a lead disc with a hole in the center was placed in the light path and the transmission at this particular wave length was noted. To re-establish at a later time the conditions under which I_o measured 100%, it was only necessary to place the attenuator in the light path and adjust the amplifier gain until the intensity was again the same as originally observed with the disc in position. The optical density was then determined from the defining relation O. D. $= \log I_o / I$ and plotted against the observed pressure. For purposes of analysis the ethylene chloride absorption maximum at 8.07 microns was chosen and an absorption minimum for methanol at 9.75 microns was used. A minimum in the absorption curve for methanol was chosen rather than a maximum because the extinction coefficients at the methanol maxima were much too high to be useful at any but the lowest pressures. The results of some analyses by this method are shown in Figure 5 for methanol and Figure 6 for ethylene chloride. During the course of these experiments it became desirable to investigate the effect of slit width on the measured optical density. Figure 6 shows this for ethylene chloride. In the visible region the effect of slit width is usually not nearly so critical, but because infrared absorption bands are often quite narrow, it was found absolutely imperative that the same size slit width be used for all measurements. It was always observed that at an absorption maximum the extinction coefficient increased as the light became more nearly monochromatic. Hence the extinction coefficient decreased with increasing slit width.

Measurement of Optical Density at Constant Total Pressure. It was observed during the early experiments that if the total pressure in the cell was increased by the admission of a second gas, even an optically transparent gas like nitrogen, then the optical density of the absorbing gas was increased. This effect has been observed by others and is discussed in a paper by Wilson and Wells (70). Hudson (22) has found that although strictly speaking the change in optical density depends on the nature of the added gas, a very good approximation of the effect of most gases could be obtained by measuring the effect of adding some simple gas like nitrogen. Since in the analysis of real ternary solutions, it was recognized that the total pressure would not be constant, it was decided to measure the optical densities of methanol and ethylene chloride at various partial pressures, enough nitrogen being added to bring the total pressure to some predetermined value (in this case 122 mm Hg).

Figure 5

Optical Density vs Pressure

Methanol $\lambda = 9.75\mu$ (min) P_t variable

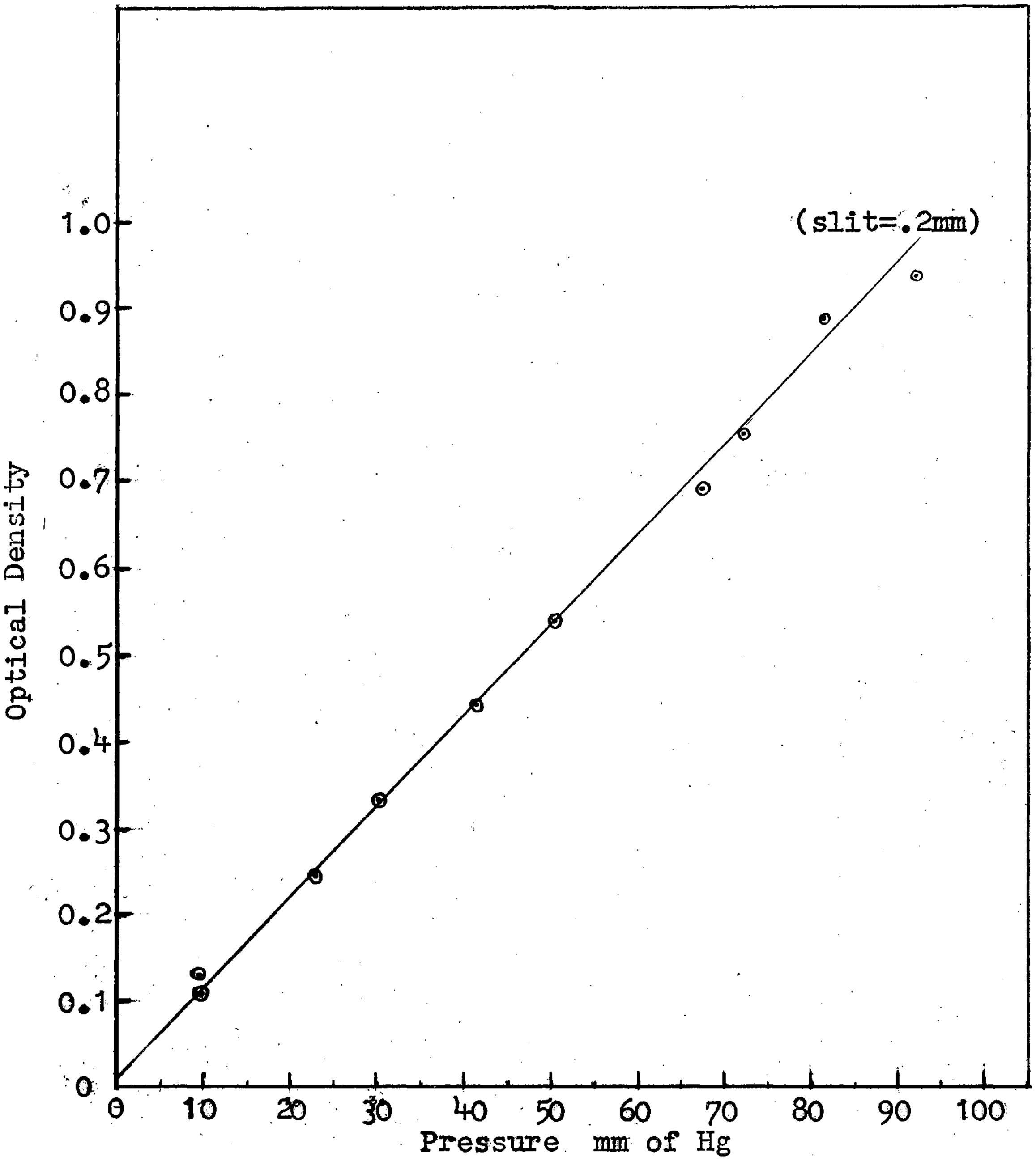
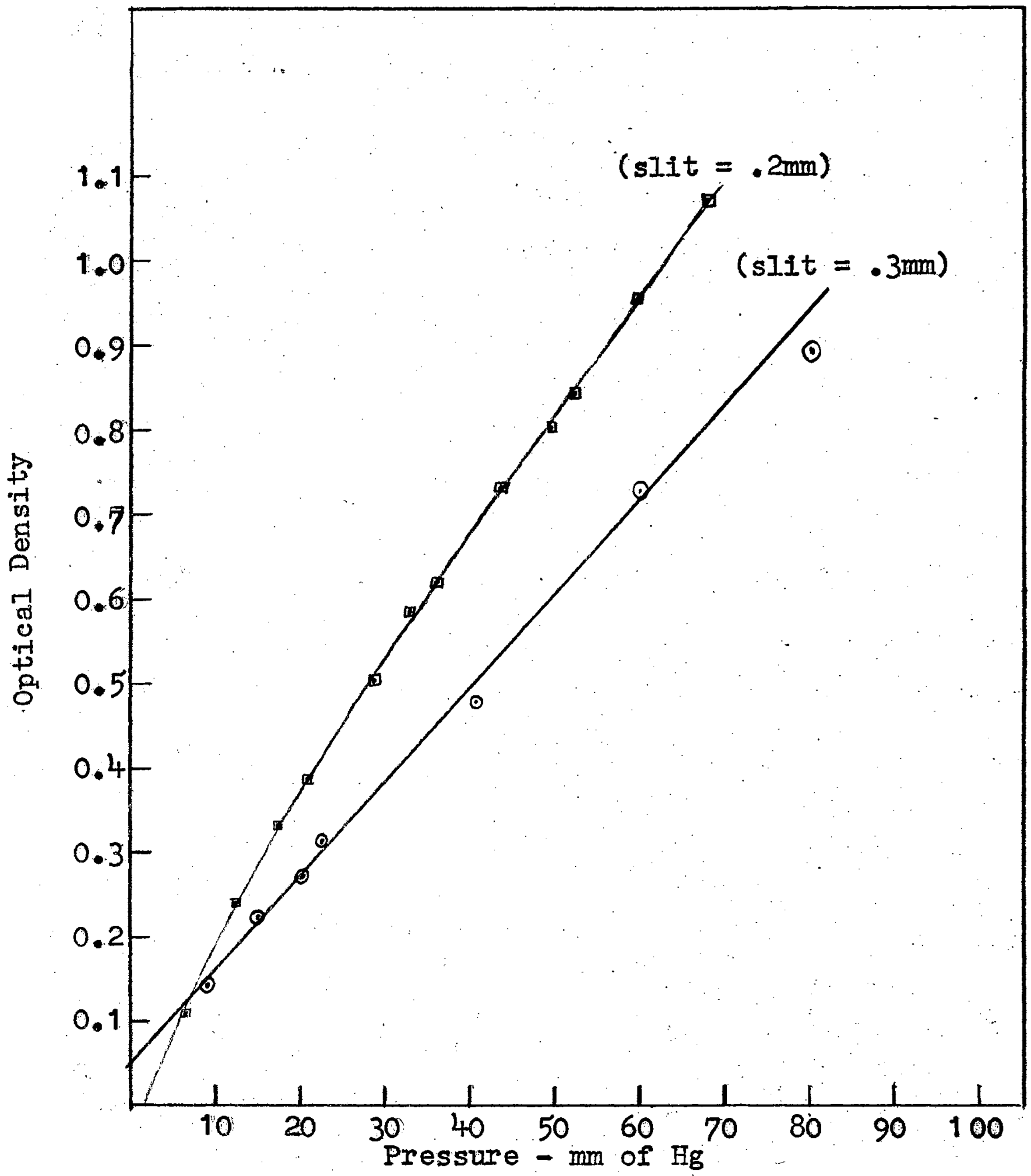


Figure 6

Ethylene Chloride $\lambda = 8.07\mu$ (max) P_t variable

Optical Density vs Pressure



Since there was positive evidence of adsorption of the organic vapors by the stopcock lubricant throughout the system in quantities sufficient to affect the optical density, a new all metal system (Figure 2) was constructed, replacing all the lubricated stopcocks by bellows-sealed vacuum valves. A technique was devised whereby the cell could be filled to some known pressure with the organic vapor, and then nitrogen admitted until the total pressure was 122 mm Hg. The optical density was determined in precisely the same manner as previously described. The results of analyses carried out in this manner are summarized in Figures 7 and 8. It was noted that although the results were considerably better than with the first method, at optical density values greater than unity very serious deviations from Beer's law occurred, especially for methanol. It was suspected that the apparent deviation from Beer's law was actually caused by instability and drift in the spectrometer or recorder amplifier. It should be pointed out that at optical density values of around 1.0 a recorder drift of one scale division (and this was not unusual) introduced an error of 10% or more in the transmission value. To avoid the difficulties associated with the limited range of measurable optical densities and the instability of the recorder, it was decided to by-pass the recorder and to measure the output of the spectrometer directly with a high precision potentiometer. The potentiometer, besides eliminating the instability associated with the recorder, effectively increased the range of measurable optical densities by a factor of at least 10. For example, with the recorder $\underline{I}$ could be measured to only 1/500 of $\underline{I}_o$, whereas with the potentiometer $\underline{I}$ could be measured to about 1/5,000 of $\underline{I}_o$. Another series of measurements were made on methanol using the potentiometer instead of

Figure 7

Optical Density vs Pressure

Ethylene Chloride $\lambda = 8.07\mu$ $P_t \sim 122$ mm of Hg

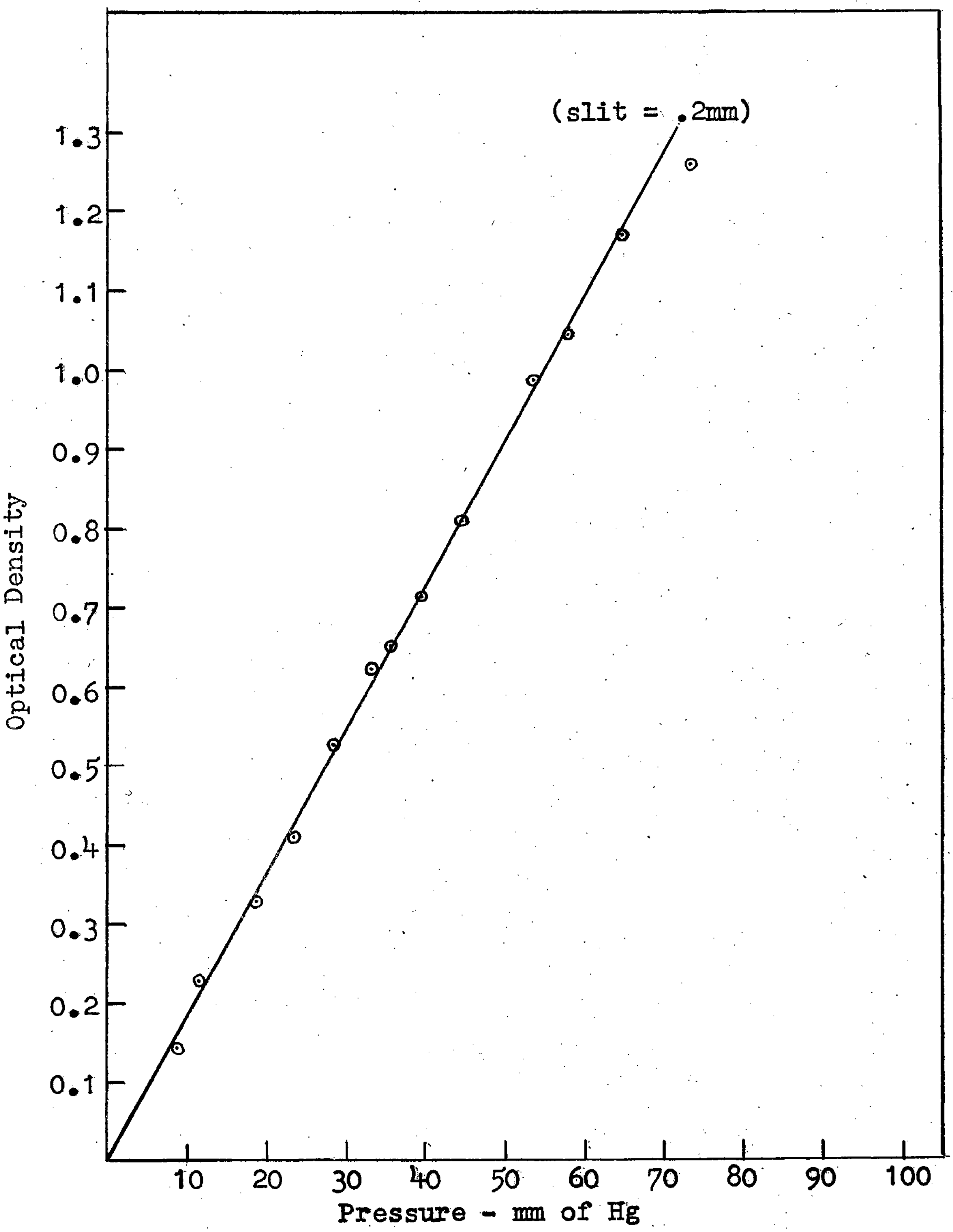


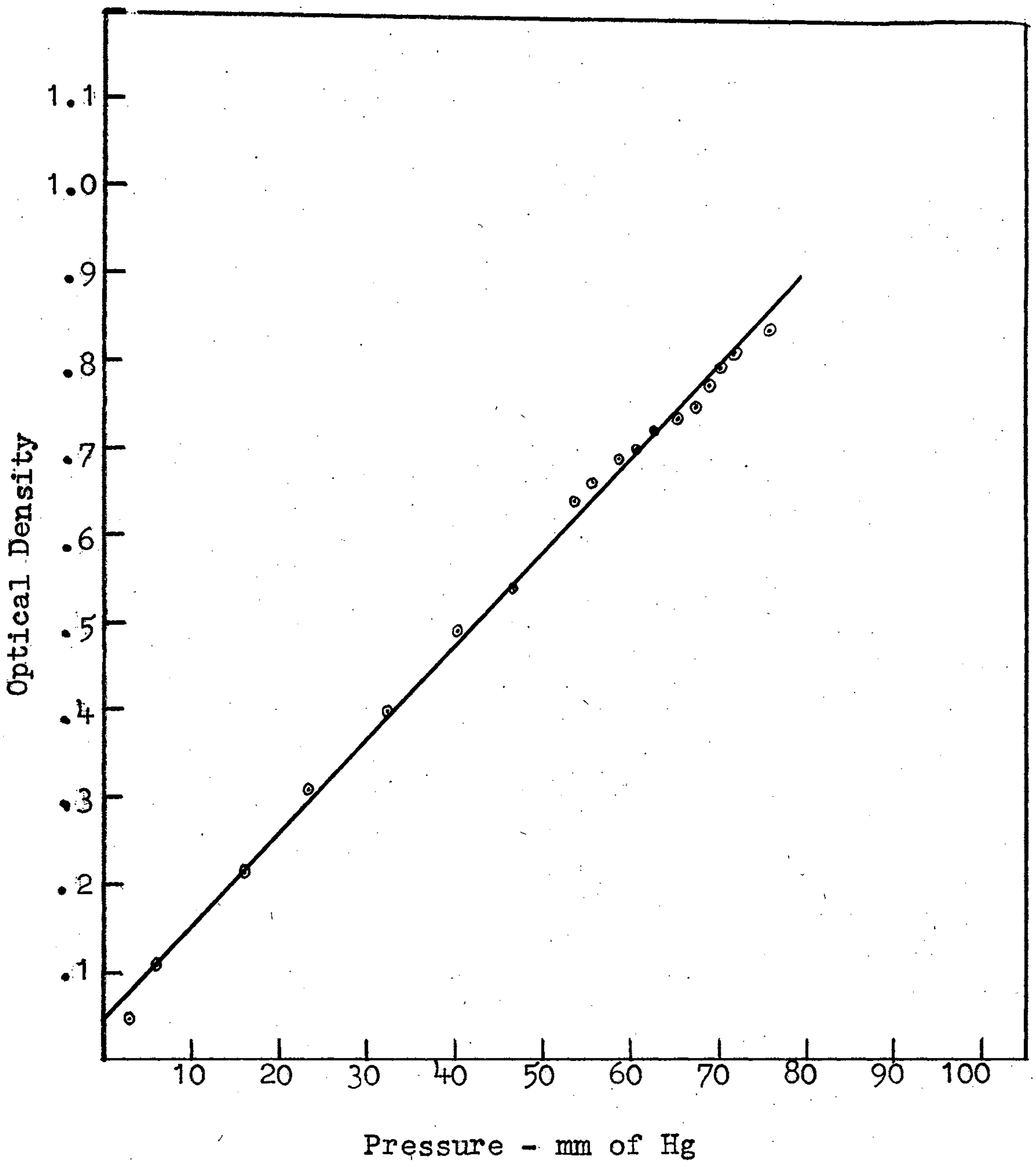
Figure 8

Methanol $\lambda = 9.75\mu$ (min)

$P_t \sim$ 122mm

Temp = 37° C

O. D. via L & N Recorder



the recorder to measure the signal from the spectrophotometer. The results of these analyses are shown graphically in Figure 9.

Comparison of Figures 8 and 9 shows the tremendous advantage gained by the use of the potentiometer in measuring high optical densities. Although methanol did not follow Beer's law exactly over the entire investigated pressure range, its partial pressure $\underline{p}_1$ could be determined from a working curve with an accuracy of about ± 2.0%.

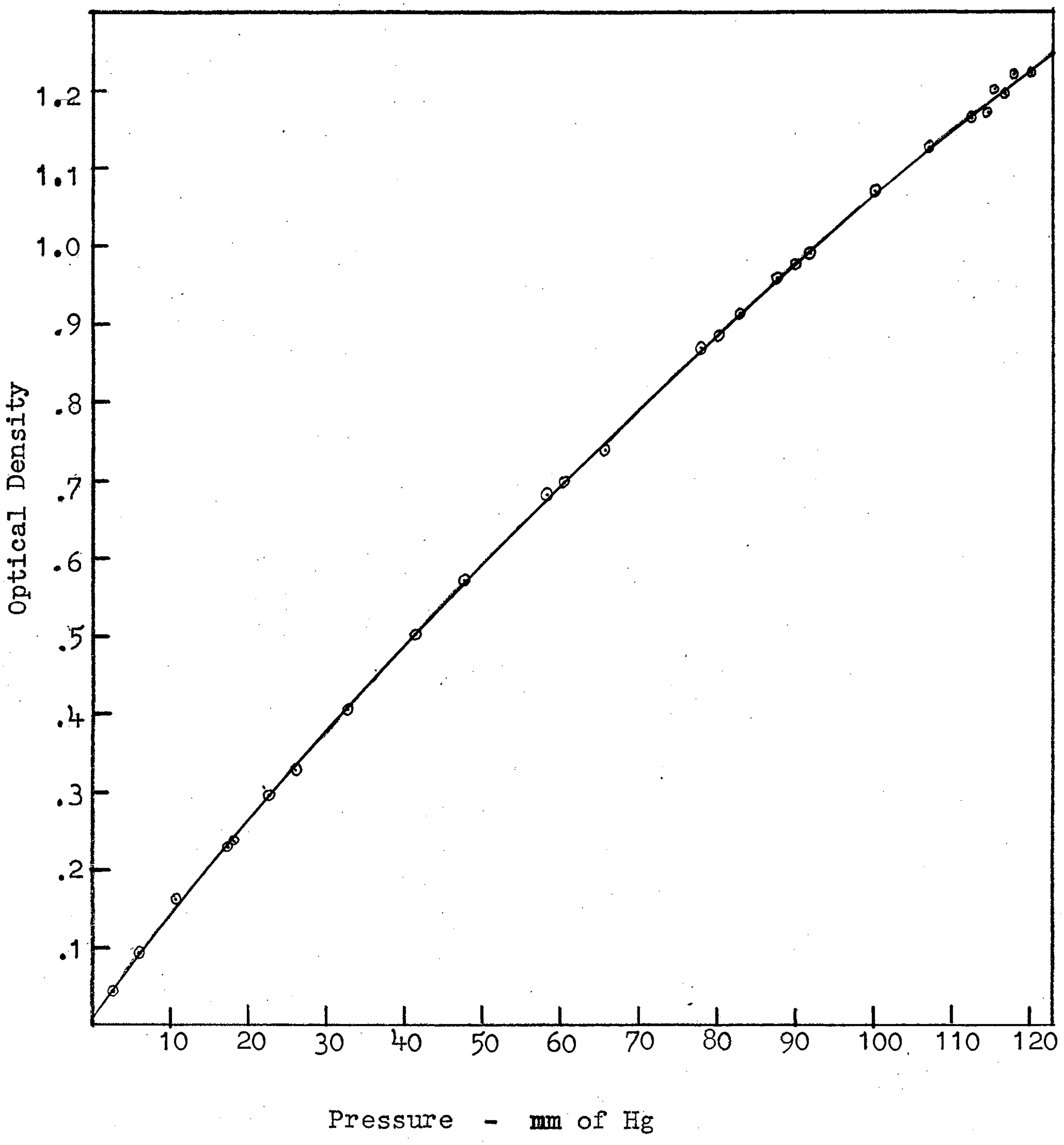
Experimental Difficulties Encountered in Vapor Phase Analyses. Although the best measurements in the gas phase showed some promise of being useful, there was still observed an unexplained increase in transmission with the length of time that the cell remained on the spectrometer. A series of experiments were performed to see if decomposition of the vapor, shift of absorption maximum or incomplete mixing of the vapors was responsible for this. No evidence could be found which indicated that decomposition or shift in position of absorption maxima occurred to an extent sufficient to cause the observed change in optical density with time. Thorough mixing did, in fact, have some effect on the optical density, but an undesirable increase in transmission with time was still observed even after vigorously shaking the cell into which fifteen one-half inch square pices of silver foil had been added. It was also noted that the silver chloride windows were not at all optically homogeneous and, therefore, positioning the cell in precisely the same location in the light path was absolutely imperative if reliable results were to be obtained.

Although it is conceivable that the gas-phase method of analysis might be made to work, it was apparent that it would require entirely too much attention to myriads of minute details to be really practical.

Figure 9

Methanol $\lambda = 9.75\mu$ (min) Temp = 37°C

$P_t \sim$ 122mm O. D. via Potentiometer



This was true both with respect to the operation of the instrument itself and to the process of collecting the sample for analysis. It was for this reason, mainly, that further work with the gas phase method was discontinued in favor of a much simpler technique.

Liquid Phase Analysis in the Medium Infrared Region.

Advantages. Since the analysis of gases presented so many difficulties, it was decided to investigate the possibility of analyzing the equilibrium vapors in the liquid phase by first quantitatively condensing the vapors and then dissolving them in carbon disulfide, which is practically transparent to infrared radiation. It was expected that this method would eliminate some of the more serious difficulties encountered in the vapor phase procedure. Some important advantages to be gained by liquid phase analysis were:

1) Elimination of the need for a suitable gasket material for the gas cell.

2) Elimination of the problem of mixing vapors.

3) Elimination of pressure control difficulties. (Careful control of the final pressure was necessary with the gas phase method.)

4) Ability to work in the concentration range which offered maximum accuracy.

Analyses. It can be proved that maximum analytical accuracy in spectrophotometric analyses occurs when the transmission is 37%. A few preliminary experiments with the standard fixed thickness liquid cell (1 mm) showed that this condition resulted when the concentrations of methanol and ethylene chloride were 0.10% and 0.22% by weight respectively. Although one could not, of course, control the ratio of the components in the equilibrium vapor, it was possible to add sufficient carbon disulfide to the condensed liquid to make the concentration of one of the components fall in this optimum concentration range.

Solutions of various known concentrations of methanol in carbon disulfide were prepared and the optical density was determined at $\lambda = 10.2$ microns. The results are shown in Figure 10. Similar determinations were made for ethylene chloride at $\lambda = 14.3$ microns and these results are shown in Figure 11.

After many analyses had been made with the same liquid cell, it was observed that the standard curve could no longer be reproduced and that all of the later values fell above the earlier ones, i.e. after continued use of the same cell for long periods of time, the optical density gradually increased for solutions having the same concentration. This was observed for both compounds and the magnitude of the deviation was about the same for each. It was apparent that continued use of the cell had resulted in a slight dissolution of the sodium chloride windows, thereby increasing the path length of the cell. Thus it was obvious that a standard curve could not be obtained which would be useful for any great length of time. It was found, however, that the method could still be employed if certain modifications were made. Even though Beer's law did not hold exactly over the entire concentration range, it was followed very closely over any narrow range. Consequently, if two standards were run with each unknown, one of slightly greater and one of slightly smaller concentration, then the unknown concentration could be determined quite accurately. A serious disadvantage to this method was that it required at least three analyses for every unknown. However, after the acquisition of the near-infrared spectrometer, the results of preliminary experiments indicated that this instrument would be vastly

Figure 10

Optical Density vs Concentration

for Methanol at $\lambda = 10.2\mu$

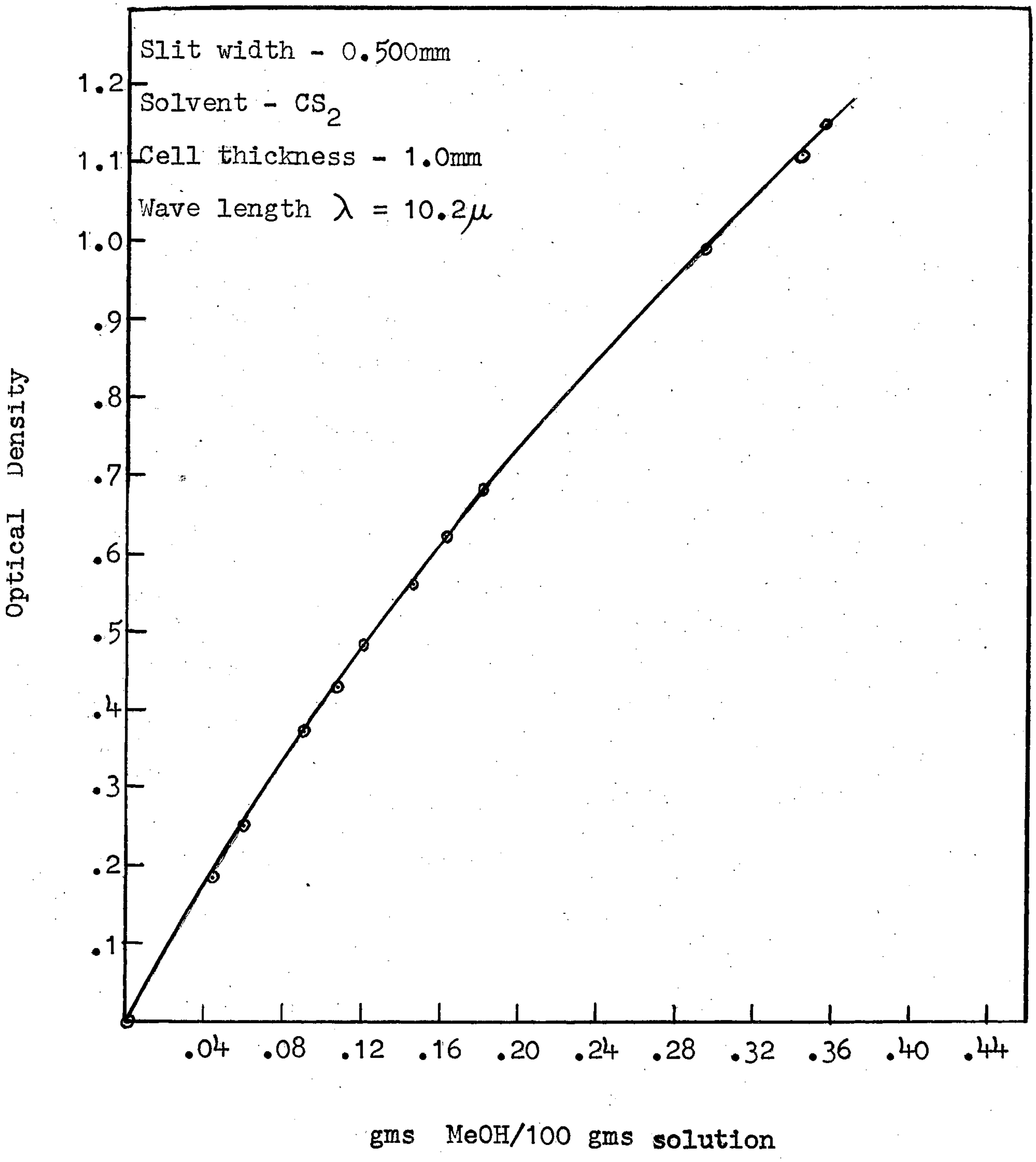
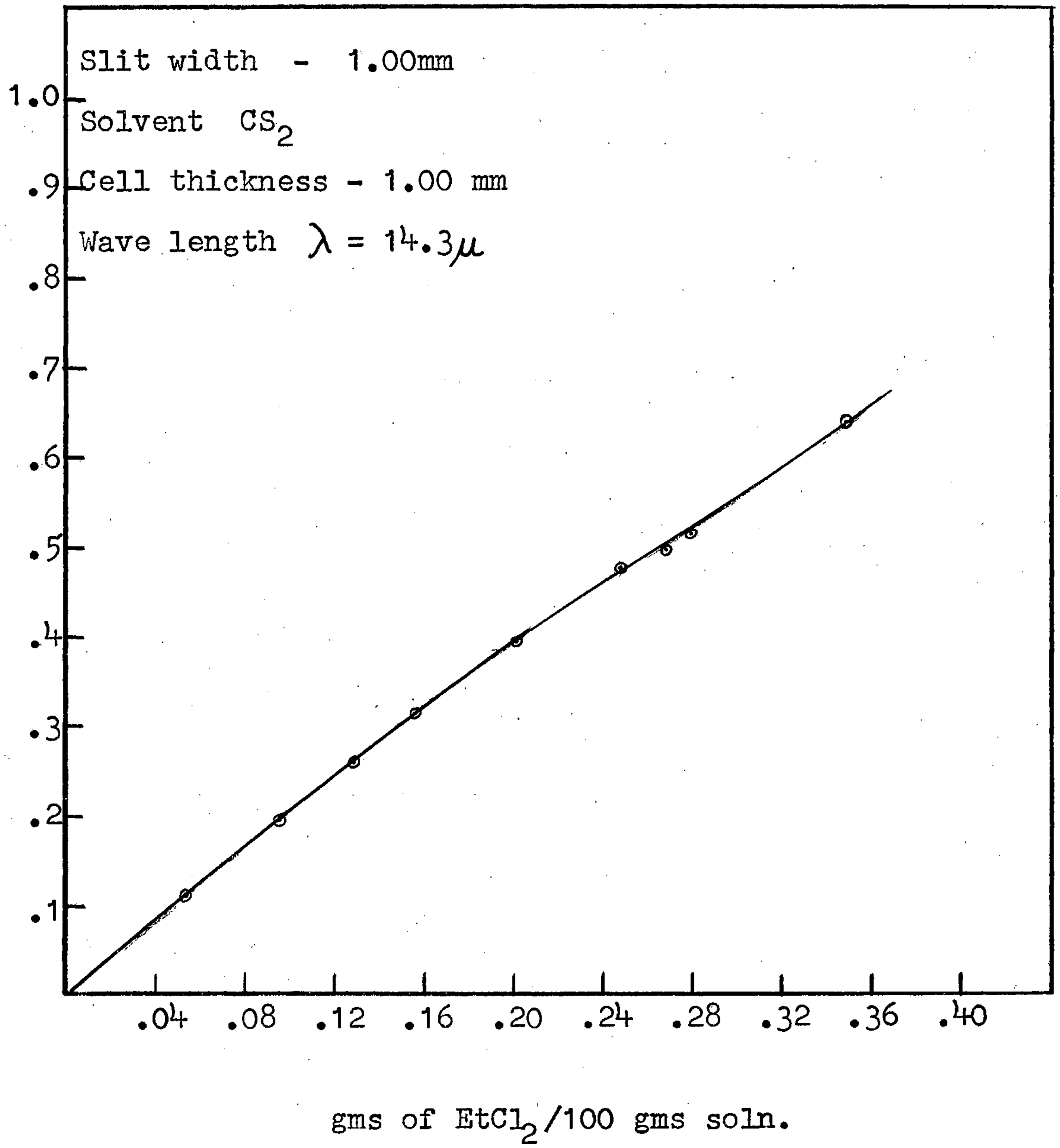


Figure 11

Optical Density vs Concentration

for Ethylene Chloride at $\lambda = 14.3\mu$



superior for the proposed analysis, and all further experiments with the model 12-C medium-infrared spectrometer were discontinued.

Effect of Scattered Light. At the very long wave lengths ($\lambda = 14.3$ microns) and the correspondingly wide slit widths used in these measurements, the problem of scattered or stray light became quite important. At high optical densities it accounted for 15% to 20% of the total signal. Fortunately the scattered light could be measured and corrected for in the following manner. The 1 mm sealed cell was first filled with carbon disulfide and the $\underline{I}_o$ value read from the potentiometer. Then the cell was filled with pure ethylene chloride (or methanol depending on the wave length in question) and the value of $\underline{I}$ was again read from the potentiometer. The 1.0 mm light path of pure component was sufficient to absorb virtually all of the light of the frequency used for analysis, but would allow light of all other wave lengths through. Some of this was scattered light and contributed to the values of $\underline{I}_o$ and $\underline{I}$. This amount of scattered radiation had to be subtracted from both $\underline{I}_o$ and $\underline{I}$ before true optical densities could be determined. To give an idea of the magnitude of the contribution of scattered light to the total signal, the following values were obtained: at 14.3 microns, $\underline{I}$ (scattered) = 2.4% of $\underline{I}_o$ and at 10.2 microns, $\underline{I}$ (scattered) = 0.24% of $\underline{I}_o$.

Liquid Phase Analysis in the Near-Infrared Region.

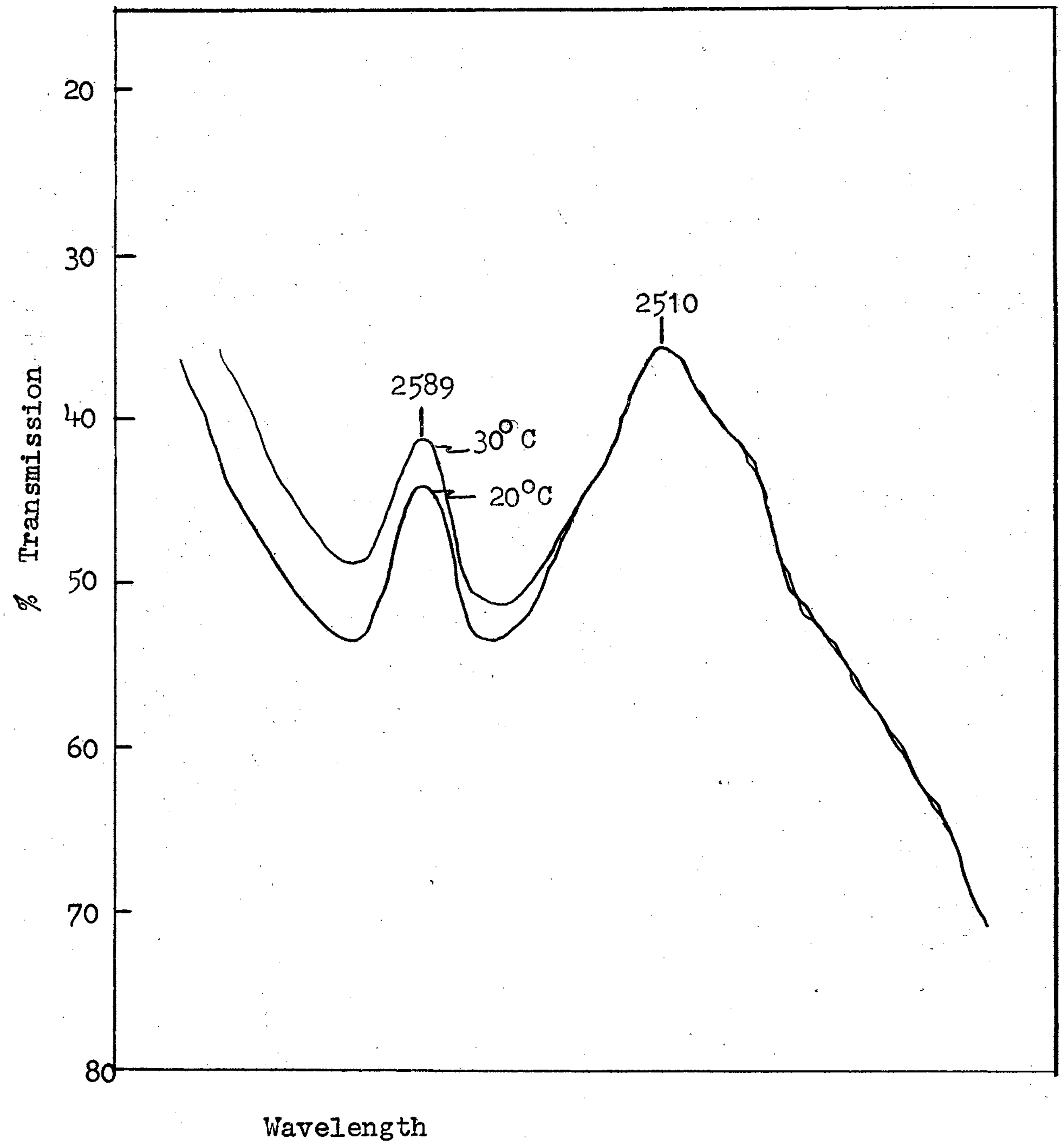
Preliminary Investigations. Solutions of about 2.0% by weight of both methanol and ethylene chloride, in carbon disulfide were prepared and the spectrum from 3.5 to 0.9 microns was obtained. Both compounds showed fairly strong absorption bands suitable for analysis. Methanol showed several well defined bands at 1394, 2266, 2517 and 2589 millimicrons. Ethylene chloride showed strong bands at 1706 and 2341 millimicrons.

Adherence to Beer's law was tested for the compounds at the above wave lengths. The 1394 millimicron band for methanol is extremely narrow and did not follow Beer's law at all. This band is the second overtone of the OH stretching vibration and is greatly affected by hydrogen bonding, hence serious deviations from Beer's law could be expected. Beer's law was followed to better than 1% by methanol at the 2266 millimicron wave length, but unfortunately this wave length corresponded to a steeply rising portion of an ethylene chloride absorption band, and therefore could not be used for analysis of mixtures containing ethylene chloride. The other two bands at 2517 and 2589 millimicrons showed a linear relationship between concentration and optical density to within about 2%. Ethylene chloride, however, followed Beer's law to better than 1% at both 1706 and 2341 millimicrons. All factors considered it appeared as if the 2589 millimicron peak and the 1706 millimicron peak would be the most suitable for the analysis of methanol and ethylene chloride respectively.

In the process of preparing a standard curve for methanol in carbon disulfide at 2589 millimicrons, two phenomena were observed which, it was felt, could seriously affect the accuracy of the measurements: 1) Methanol apparently catalyzed the photochemical decomposition of carbon disulfide. This was indicated by the fact that after standing for 24 hours the solutions took on a very slight brownish cast, the intensity of which increased with the concentration of methanol. 2) The extinction coefficient of the 2589 millimicron band increased with temperature. The shape of the band at 20° and 30° is reproduced in Figure 12. There are several theoretical explanations for this peculiar behavior, but these need not be discussed here. It was observed, however, that

Figure 12

Effect of Temperature on Transmission of Methanol at 2589 and 2510 millimicrons



the adjacent peak at 2517 millimicrons was not at all affected by this temperature variation. Hence it was decided to use the methanol peak at 2517 millimicrons for subsequent analyses. Since carbon disulfide is undesirable to work with for many reasons, carbon tetrachloride was investigated as a possible solvent. It proved to be an exceptionally fine solvent for work in the near infrared. It showed a small absorption peak at about 2700 millimicrons but was absolutely transparent from 2650 millimicrons to beyond the visible region. All subsequent work, therefore, was done using carbon tetrachloride as the solvent. The spectra of methanol and ethylene chloride in carbon tetrachloride were then obtained. Each spectrum was found to be practically identical with that observed in carbon disulfide. The 1706 millimicron peak was shifted slightly to 1703 millimicrons, and the 2517 millimicron peak was shifted to 2510 millimicrons.

Preparation of Solutions and Standard Curves. Standard curves were drawn for methanol and ethylene chloride solutions in carbon tetrachloride, and conformity with Beer's law to better than 1% was found over a wide concentration range. However, to obtain this degree of accuracy certain precautions had to be strictly observed:

1) The reference energy had to be the same for all measurements. This was accomplished by adjustment of a potentiometer inside the instrument.

2) The slit width had to be the same for all measurements at a particular wave length. Once the slit was set at some value at a given wave length the slit servo controlled its dimensions at all other wave lengths.

3) I_o had to be recorded for each analysis because the instrument

would not retain a given $\underline{I}_o$ value for any great length of time, contrary to the company literature. Possibly the instability of the campus electrical voltage was responsible for this behavior, because the instrument was observed to be much more stable at night and in the early morning hours, than during the day.

4) The use of special liquid cells of the type described earlier was necessary to prevent evaporation.

5) Extreme care had to be exercised to keep small particles of lint or dust out of the cells because when such particles drifted into the light path they caused false transmission values to be obtained.

The final standard curves for methanol and ethylene chloride are given in Figures 13 and 14. The instrument operation conditions and the equations of the curves accompany the graphs.

In the preparation of the solutions for use as standards, the special teflon-stoppered vials described earlier were used and the following procedure followed. A concentrated stock solution (ca.6-8%) was first prepared by injecting about 3-4 grams of the organic liquid into a small-neck 40 ml vial by means of a hypodermic syringe. The vial was immediately capped, and after weighing was immersed in a "dry" ice-acetone bath to chill the contents and reduce its vapor pressure. About 50 grams of carbon tetrachloride were then admitted into the vial, and after room temperature had been reached, the entire assembly was again weighed. The actual working standard solutions were prepared by weighing a certain amount of the stock solution into the 10 ml vials described earlier, followed by freezing and diluting as described above. The freezing technique involving the use of small vials was absolutely necessary, because when larger vials were used without freezing a

Figure 13

Methanol (2510 millimicrons) & (1703 millimicrons)

Instrument Settings:

λ = 2510 , slit = .070 mm

λ = 1703 , slit = .030 mm

$$\overset{2510}{\text{O. D.}} = 0.4195\ C + 0.0140$$

$$\overset{1703}{\text{O. D.}} = 0.0623\ C \pm 0.000$$

Energy 17.5 volts

Transmission 0 - 100 %

Chart 1"/min Drive # 100

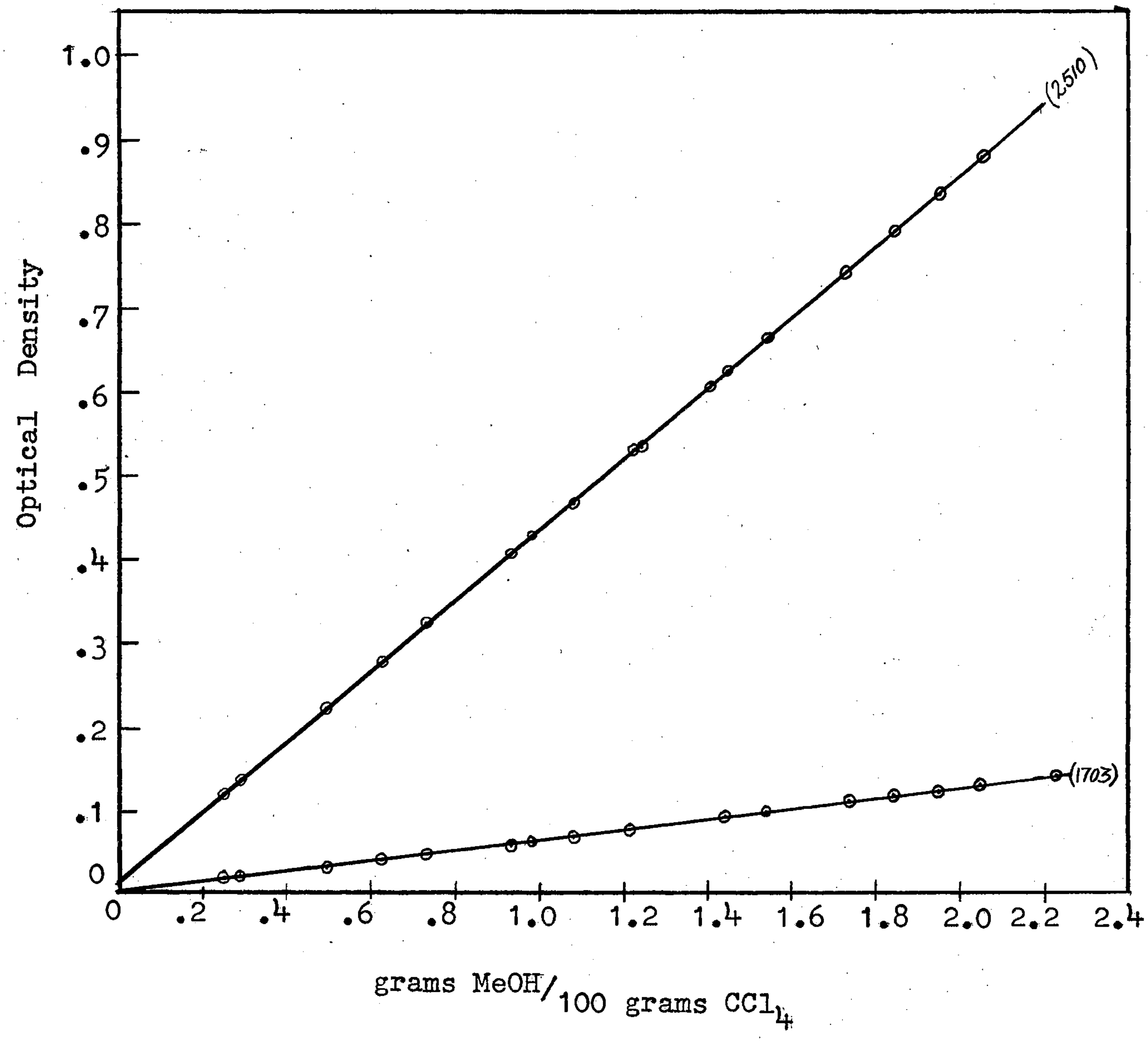


Figure 14

Ethylene Chloride (1703 millimicrons)&(2510 millimicrons)

Instrument Settings:

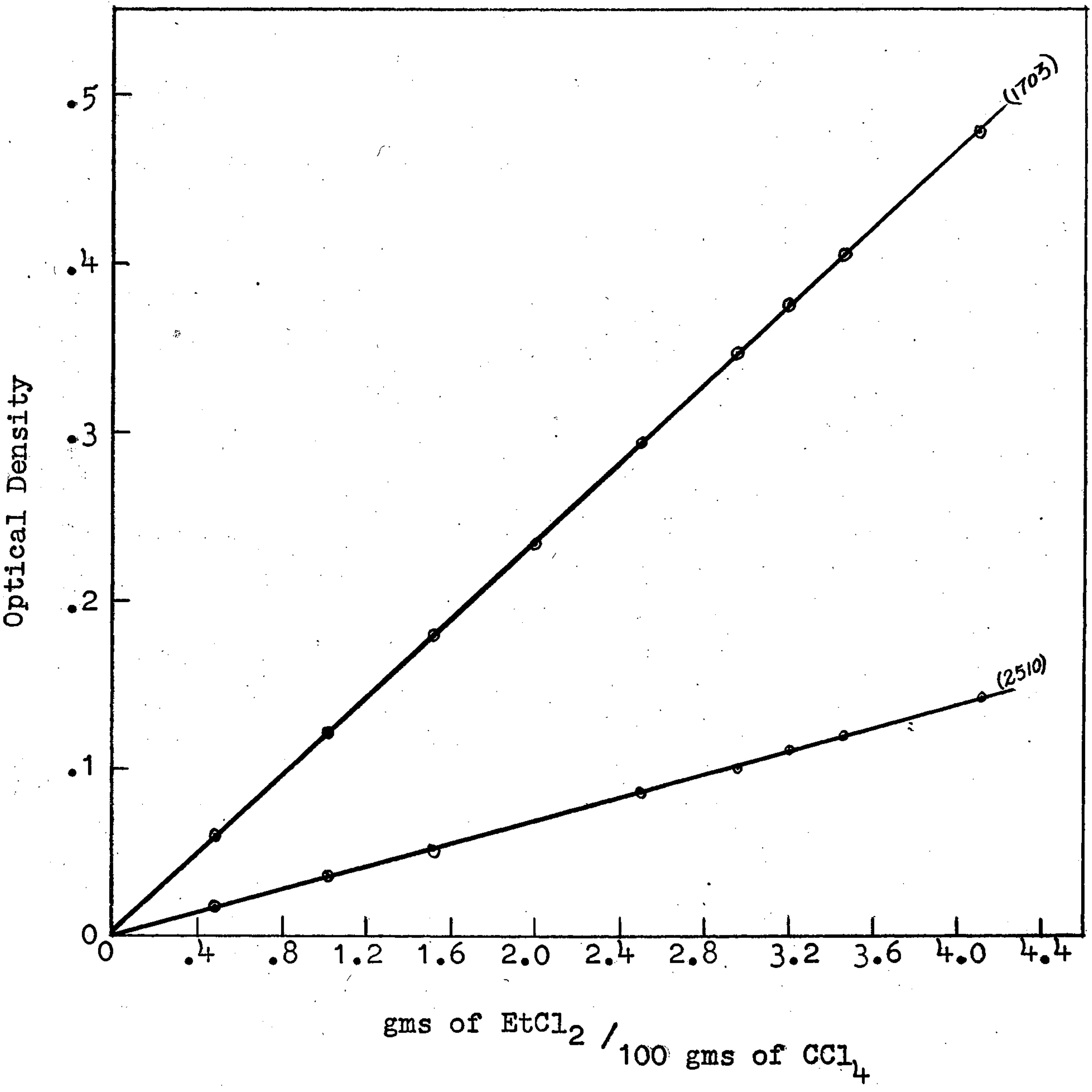
λ = 2510 , slit = .070 mm } in air
λ = 1703 , slit = .030 mm }

Energy = 17.5 volts

Transmission 0 - 100 %

Chart 1"/min Drive # 100

Equations
1703
O. D. =0.1173 C + .0010
2510
O. D. =0.0341 C + .0015



significant amount of methanol escaped when the vials were opened to admit the carbon tetrachloride. It should be pointed out that even in very dilute solutions of methanol in carbon tetrachloride, the methanol exerts approximately the same partial pressure as does the pure liquid (63).

Analysis of Mixtures of Known MeOH / $EtCl_2$ Ratio. As was indicated earlier on page 8, in order to determine p_1 and p_2 it was necessary to know only P_t and a ratio of the concentrations of methanol and ethylene chloride. A set of experiments were therefore performed to determine if the ratio, MeOH / $EtCl_2$, could be accurately determined. Solutions of several different ratios of MeOH / $EtCl_2$ were prepared ranging from 0.37 to 2.0 on a weight basis. Several concentrations at each ratio in carbon tetrachloride were prepared by injecting a few tenths of a milliliter of the prepared mixture of methanol and ethylene chloride, below the surface of the carbon tetrachloride in an almost completely filled 10 ml vial. The optical densities were then determined at 1703 and 2510 millimicrons. By the use of a combination of Equations (57) and (58) (which will be derived later) the ratio was calculated. It was found that the ratio could be determined with an average error of only about 0.5% over the range measured. Since both compounds are analyzed together, any systematic or instrumental errors will tend to affect both compounds to the same extent and any error thus introduced will be minimized when the ratio of concentrations is found. Hence the ratio of concentrations can often be determined more accurately than the concentration of either pure component alone.

Vapor Pressure of the Pure Compounds at 25°.

To test the accuracy of the apparatus and also to obtain reliable

$\underline{p}^{o}$ values for methanol and ethylene chloride at 25°, the vapor pressures of both of these compounds were determined. Reagent grade methanol or ethylene chloride, purified in a manner to be described later, was placed in the 125 ml Florence flask $\underline{FF}$ Figure (3) and a vacuum was applied to the system until about 10 ml of the liquid had distilled off. Valves $\underline{V}_1$ and $\underline{V}_2$ were then closed and the receiver $\underline{R}$ was frozen with a "dry" ice-acetone mixture. The pressure indicated by the manometer was then noted. Almost always the pressure would drop to <0.1 mm of Hg indicating that essentially all of the air had been removed from the sample. If the manometer indicated the presence of any appreciable amount of air, e.g. pressure >0.1 mm of Hg, the entire system was brought to room temperature and evacuated while a few more milliliters of liquid were distilled under vacuum. This procedure was repeated until the manometer indicated <0.1 mm of pressure (the vapor pressure of MeOH at - 78° C is about 0.04 mm.). When the system had been completely freed of air the entire apparatus was submerged in a constant temperature bath at 25.00 ± 0.01° for an hour or so with periodic stirring until the pressure, as indicated by the manometer, became constant. About 10 readings for each pure liquid were made. After each measurement a milliliter or two of liquid was removed by vaccum distillation to see if possibly a more volatile impurity was being removed or a less volatile impurity was being concentrated. No trends in the pressure readings were observed, however. The vapor pressure readings were consistent to within ± 0.1 mm which was the limit of accuracy of the cathetometer. Methanol obtained from two different companies was used and the results were the same. The values obtained were corrected to 0° C and were found to be:

Methanol 126.6 mm (Hg at 0° C)

Ethylene Chloride 78.7 mm (Hg at 0° C)

Literature values for the vapor pressure of methanol at 25° differ considerably, but the more recent values are quite close together. The following values were taken from the literature:

I. C. T.	(24)	122.4 mm
Pesce	(52)	124.4 mm
Dreisbach	(11)	126.4 mm
Niini	(46)	126.5 mm
This Work		126.6 mm
Dever	(9)	127.1 mm

For ethylene chloride the Handbook of Chemistry and Physics (20) gives the value of 78.8 mm.

<u>Binary System</u>: $CoCl_2$ - MeOH.

Since it was desirable to relate the activities of $CoCl_2$ in the ternary system to some convenient reference state in the binary system, the vapor pressure isotherm was obtained for the system $CoCl_2$ - MeOH from pure methanol to the saturated solution.

<u>Preparation of Solutions</u>. The binary solution was prepared in the following manner. Anhydrous $CoCl_2$ was weighed into the 125 ml Florence flask <u>FF</u> (Fig. 3), and the flask was immediately stoppered. Freshly distilled methanol was then admitted, and the flask was reweighed to determine the amount of methanol added. The alnico stirrer was introduced and the flask was connected to the apparatus. After all the salt was dissolved, the solution was subjected to a degassing procedure as follows. With $\underline{V}_2$ closed, the entire system was evacuated.

Valve $\underline{V}_1$ was then closed and $\underline{V}_2$ opened, allowing most of the air and some methanol vapor to expand into the system. When the pressure stopped increasing as indicated by the manometer, $\underline{V}_2$ was closed and a "dry ice" - acetone bath was placed around the reciever R causing the methanol to condense in the receiver with a resultant decrease in pressure. After standing a few minutes $\underline{V}_1$ was opened and the air was removed by evacuation leaving the methanol condensed in the receiver. After all the air had been pumped out, $\underline{V}_1$ was closed, $\underline{V}_2$ was opened, and again air and methanol was allowed to expand into the system. This process was repeated until, upon chilling the receiver R, the McLeod gauge read only 0.04 mm (the vapor pressure of methanol at this temperature.). At this point there were about 5 - 8 grams of methanol precipitated in the receiver which had to be returned to the flask FF if the concentration was to remain unchanged. This was easily accomplished by cooling FF with ice or "dry" ice-acetone mixture and warming the receiver until its contents had distilled into FF.

Vapor Pressure of the Solutions and Methanolates. After the degassing procedure was completed, the entire apparatus was immersed in the constant temperature bath and the pressure read from the manometer after equilibrium was attained. To obtain a new concentration, about 10 grams of methanol were distilled into R and chilled with "dry" ice-acetone. The receiver R was removed from the apparatus, stoppered, thawed, and weighed. The amount of methanol contained in R was subtracted from the initial weight of methanol in FF and the new concentration determined. Using this technique it was unnecessary to prepare and degas a new solution each time the concentration was changed. However, as a matter of precaution no more than three concentrations were derived from any single original solution. The vapor pressures of 20 solutions ranging from pure methanol to saturation were measured. The method of least squares was applied to the data, and the following equation was obtained:

$$P_1 = 126.64 - 5.1296m - 0.5421m^2 + 0.1831m^3 - 0.04515m^4 \qquad (21)$$

where m = molality. (The results are shown graphically in Figure 15.) Although no direct comparison with the literature could be made, Lloyd (35) reported that the saturated solution of $CoCl_2$ in methanol contains 43.6 grams of $CoCl_2$ per 100 grams of methanol at 25°. In reasonably good agreement with this value it was found that the experimental vapor pressure curve intersects the constant pressure line (saturated solution) at 44.1 grams of $CoCl_2$ per 100 grams of methanol.

The vapor pressures of the various solid methanolates were also determined with the apparatus. The solid phase in equilibrium with the saturated solution at 25° is reported to be the trimethanolate $CoCl_2 \cdot 3MeOH$ by Lloyd (35) and by Zvyagintsev (72). Its vapor pressure was found to be 45.0 mm. The two lower methanolates also exist at this temperature and their vapor pressures at 25° C were found to be:

$CoCl_2 \cdot 2\ MeOH$ = 39.3 mm

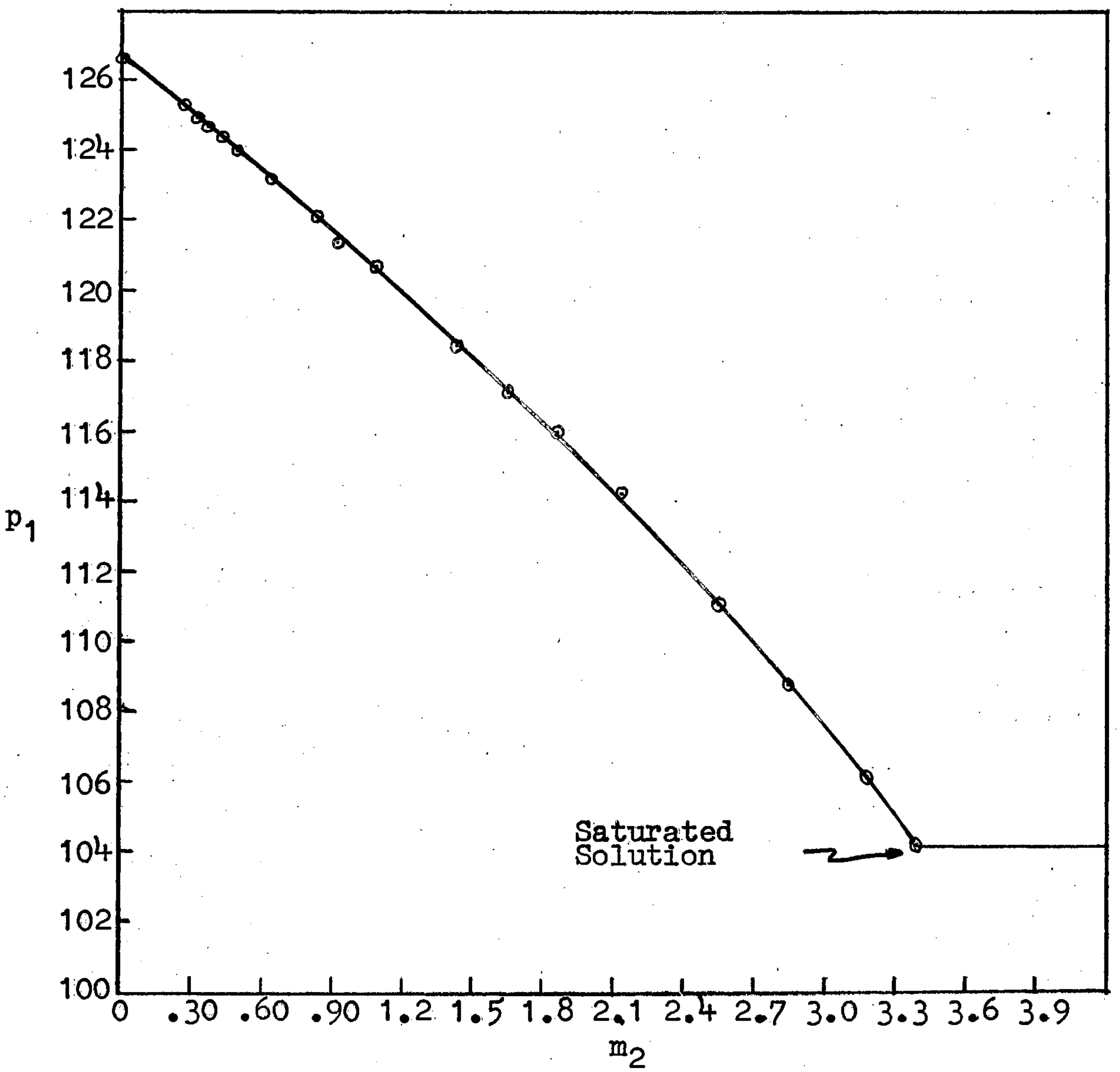
$CoCl_2 \cdot 1\ MeOH$ = 10.9 mm

The equilibrium vapor pressures were measured as follows. About 30 grams of anhydrous $CoCl_2$ were dissolved in methanol, and the solution was distilled under vacuum until it became saturated; its pressure dropped, and again remained constant, this time at 45.0 mm. Pumping was continued very carefully until the pressure again dropped. This time it took 10 minutes for equilibrium to be attained. After the system had apparently reached equilibrium, a pressure of 39.3 mm was recorded and the system was evacuated for a few more minutes. After

Figure 15

Vapor Pressure of $CoCl_2$ - Methanol Solutions

$$p_1 = 126.64 - 5.1296m_2 - .5421m_2^2 + .1831m_2^3 - .04515m_2^4$$



evacuation, the system was allowed to attain equilibrium overnight and the same pressure was recorded as previously, namely 39.3 mm. The same procedure was followed for the last methanolate, with about 12 hours being allowed for equilibrium to be attained (although 1 hour would have been sufficient). The solid $CoCl_2 \cdot 1\ MeOH$ exhibited a vapor pressure of 10.9 mm at 25° C. The vapor pressure of the anhydrous salt, of course, could not be measured.

As a matter of interest, the existence of the three methanolates was easily and beautifully demonstrated by the following experiment. A length of 15 mm O. D. glass tubing was filled with anhydrous $CoCl_2$, stoppered at one end and plugged with glass wool at the other. The tube was placed in a desiccator with about 25 ml of anhydrous methanol. The desiccator was then evacuated for a few minutes to remove most of the air and to accelerate diffusion. As methanol vapor diffused up the tube, four colored bands were formed, the deep-blue 3-methanolate, the dark-pink or rose-colored 2-methanolate, the lavender or lilac-colored 1-methanolate, and the light or sky blue anhydrous salt.

Ternary Solutions.

Preparation of the Solutions.

All of the ternary solutions were prepared at a constant MeOH / $EtCl_2$ mole ratio of 2/1, and the concentration of the third component, $CoCl_2$, was varied from zero to saturation. The constant ratio solutions were prepared by weighing out exactly 40.000 grams (1.25 moles) of methanol and 61.778 grams (0.625 moles) of ethylene chloride into a 125 ml narrow-neck vial. The neck of the vial was made from 6 mm tubing and was made with a constriction large enough to accommodate a hypodermic needle. The liquids were admitted into the flask with a hypodermic syringe. The long neck with the narrow constriction kept evaporation to a negligible value during the weighing operation and also facilitated sealing off the neck after the weighing was completed. About five such vials of solution were prepared at one time and stored until needed. The ternary solutions were prepared by weighing a certain amount of anhydrous $CoCl_2$ into the flask FF and adding to this the contents of the previously prepared vial. The flask FF was reweighed to obtain the weight of the solution added. For the more concentrated solutions it was necessary to chill the flask while adding the liquid solution in order to prevent loss of solvent, for the heat of solution of $CoCl_2$ in methanol is appreciable. Extreme care was exercised in the preparation of the saturated solution because it was important not to have more than a minute trace of the solid salt present at saturation. This was accomplished by adding extremely small portions of the 2/1 liquid solution to the saturated ternary solution until only a few hair like crystals remained.

Measurement of P_t. After the ternary solution had been prepared, the flask was attached to the apparatus and the solution was degassed in the manner described for the binary solutions. After the solution was thoroughly degassed and the liquid in the receiver had been distilled back into FF, V_2 was closed and the rest of the system was evacuated. Then with frequent stirring of the contents of FF the apparatus was immersed in the constant temperature bath for about an hour until the solution attained equilibrium with the vapor above it. Valve V_2 was then opened very slightly at intervals of approximately every 2 minutes for about 1 second or so until the pressure rose by about 5 mm. After each opening of the valve, the solution was stirred vigorously for 2 minutes until equilibrium was again attained above the solution in FF.

When, upon successive openings of $\underline{V}_2$, no increase in pressure was noted, $\underline{V}_2$ was left open, the system was allowed to equilibrate for about an hour, and $\underline{P}_t$ was recorded. The vapor pressure of $\underline{P}_t$ of fifteen solutions whose concentration varied from zero to saturation was measured, and the results are shown in Figure 16. The method of least squares was applied to the data, and the resulting equation accompanies the graph.

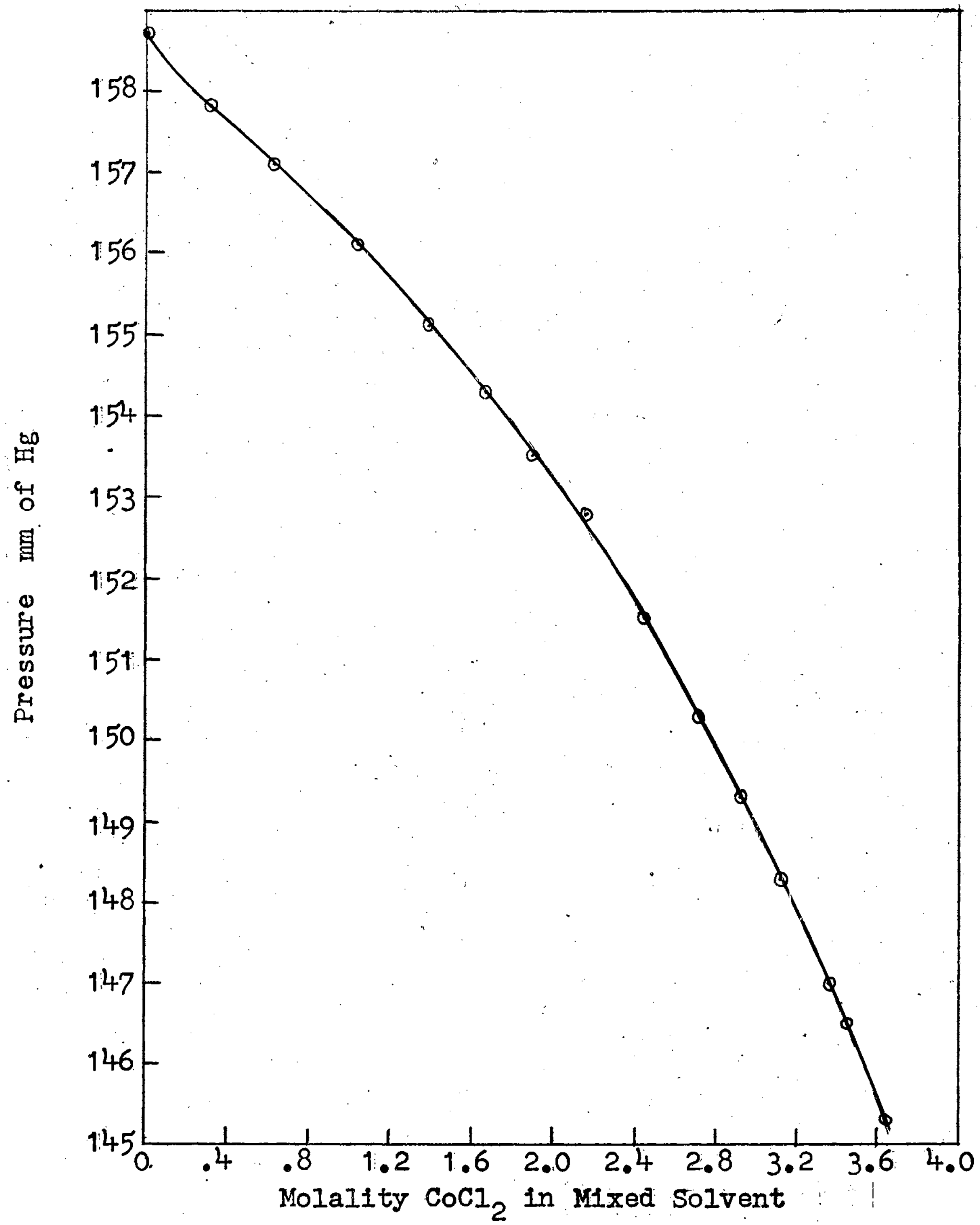
Collection of the Equilibrium Vapor. Equilibrium having been attained, and $\underline{P}_t$ having been measured, $\underline{V}_2$ was closed and the vapor in the apparatus was condensed into $\underline{R}$ by chilling the receiver with "dry" ice-acetone slush. Most of the time the system did not contain enough liquified vapors to permit them to be diluted to 10 ml and still have a concentration in the optimum analytical range; consequently $\underline{V}_2$ was opened very briefly about twenty more times at two minute intervals or until about 0.3 grams of liquid was obtained. When sufficient equilibrium vapor had been frozen, the apparatus was removed from the bath; dry air was admitted into the system through $\underline{V}_1$, and $\underline{R}$ was removed from the apparatus and stoppered. After a few more minutes of freezing, 8-10 ml of freshly distilled carbon tetrachloride were added to the frozen mixture by means of a hypodermic syringe. The receiver was stoppered, shaken, and set aside for later analysis. Liquid nitrogen was not used for the freezing-out procedure, because, although it was faster and possibly more efficient, it caused mecury from the manometer to distill over into the receiver in the form of a colloidal suspension that could be broken only by centrifuging at high speed. With "dry" ice-acteone as the refrigerant, the mercury distillation did not take place to any appreciable extent. Furthermore, the condensation was quantitative at the higher temperature.

Figure 16

Total Pressure of Mixed Vapors in the

Ternary System $CoCl_2$ - Methanol - Ethylene Chloride

$P_t = 158.7 - 2.881m + 0.6448m^2 - 0.3407m^3 + 0.02855m^4$



Analysis of the Condensed Phase. To test the reproducibility of the condensed-phase ratio analysis, three samples of the vapor in equilibrium with the binary 2/1 solution of methanol and ethylene chloride were collected as described above and analyzed. The values of the ratio agreed to within ± 0.3% which is well within experimental error. Fifteen ternary solutions containing MeOH / $EtCl_2$ in a 2/1 mole ratio and $CoCl_2$ in varying concentrations from zero to saturation were prepared. The equilibrium vapors were collected, dissolved in carbon tetrachloride and analyzed. The analysis is rather simple and performed as follows. The spectrometer was allowed to "warm up" for about one hour, and the reference energy sensitivity, slit width, time constant, chart speed, and wave length drive were all set at some definite predetermined value. The values used during these analyses accompany Figures 13 and 14. Other values of course, could be used, but the same set must be used throughout the entire work. To obtain the $\underline{I}_o$ value at a given wave length, both the reference and the sample cells were filled with carbon tetrachloride and the recorder set at 100%. Then both cells were removed leaving only air remaining in the light path. If the cells are perfectly matched at this wave length, the recorder should stay at 100%. With the particular set of cells used in these experiments the recorder went to 95.5% (which is actually extremely good matching for a pair of cells). Therefore, for all further analyses, $\underline{I}_o$ was effectively set at 100% by removing both cells and setting the recorder at 95.5%. This had to be done immediately before each analysis to insure maximum accuracy. The transmission, $\underline{I}$ of the unknown was then determined in the following manner. One cell filled with carbon tetrachloride was placed in the reference beam while the other cell containing the "unknown" was placed in the sample beam. Then a very narrow wave length range of about 10 millimicrons on either side of each absorption band was scanned at the slowest rate available with the instrument. Scanning was necessary for two reasons. First, the absorption bands were so narrow, especially for ethylene chloride, that the wave length could not be preset by hand to the exact maximum. Second, the wave length of the maximum varies slightly with concentration, being shifted toward longer wave lengths with increasing concentration. By scanning at an extremely slow rate one can easily find both the position and intensity of the absorption band. $\underline{I}$ values are read directly from the chart. Each sample was scanned three times and the average value used. Usually the curves were exactly superimposed; the greatest deviation observed for three readings was about 1%. The optical density at each wave length was found from $O.\ D. = \log I_o / I$. The ratio of concentrations was determined by a combination of Equations (16) and (17) which will be derived later. It is worthy of repeating here that the ratio can often be calculated more accurately than the actual concentration of either component alone, because all factors which may tend to cause error will probably affect both components by approximately the same amount. The results of the fifteen analyses are given in Figure 17. The method of least squares was applied to the data and the equation describing the ratio MeOH / $EtCl_2$ as a function of concentration of $CoCl_2$ accompanies the diagram.

Chemicals

Methanol.

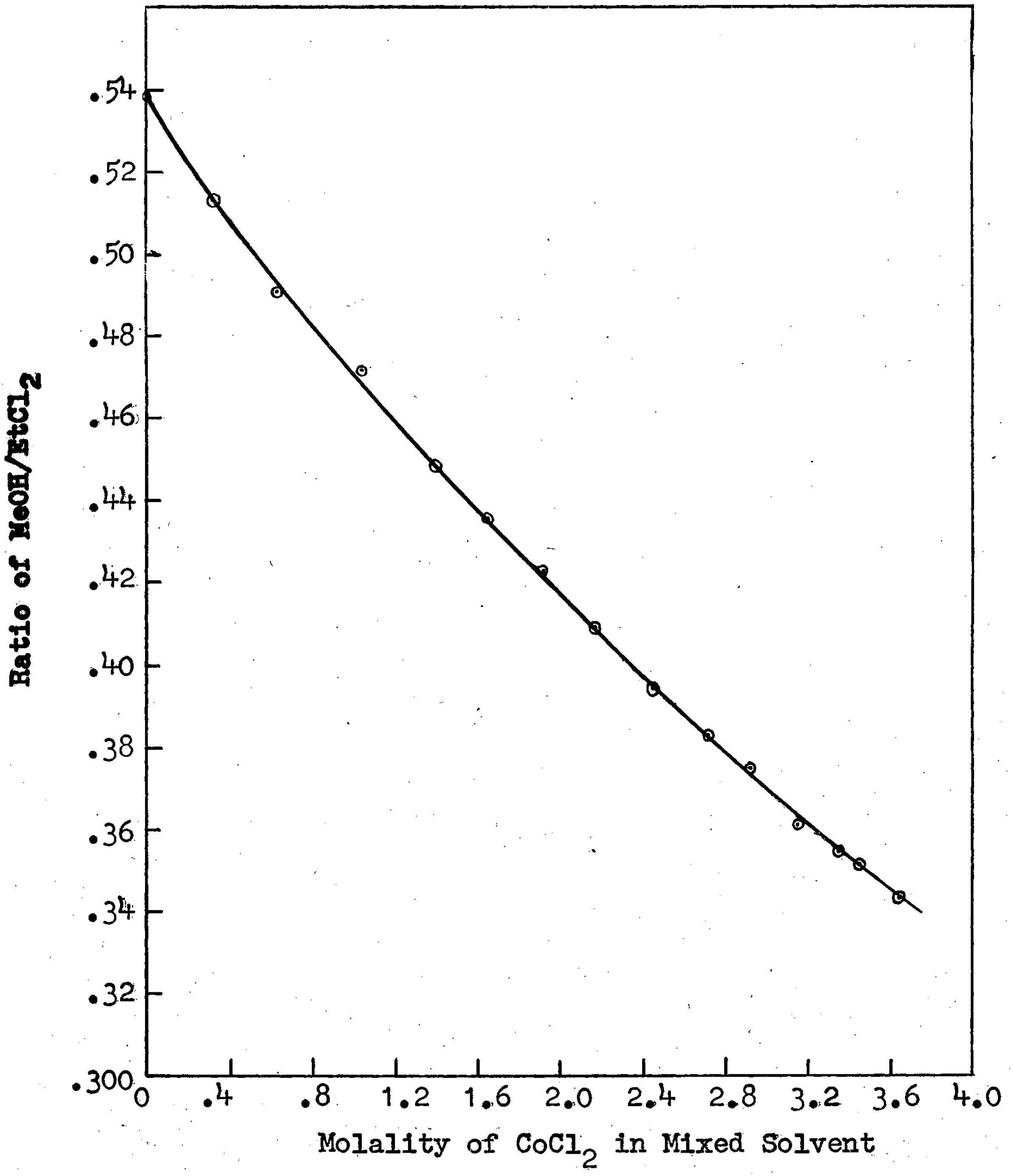
The methanol used throughout the study was Fisher Certified Reagent grade absolute methanol, "acetone-free." For the determination of the vapor pressure of the pure compound, the methanol was refluxed over

Figure 17

Ratio of MeOH/EtCl$_2$ in Equilibrium Vapor

Ternary System CoCl$_2$ - MeOH - EtCl$_2$

$\hat{R} = .5383 - .08463m_3 + .02326m_3^2 - .00726m_3^3 + .000887m_3^4$



3,5-dinitrophenylhydrazine for an hour to remove traces of aldehydes or ketones. The mixture was decanted and the methanol distilled over magnesium, according to Lund and Bjerrum, (36) to remove any trace of water. A highly efficient Todd laboratory column operated at a 10:1 reflux ratio was used to distill the product for the initial measurements. The same procedure was also used with a sample of Baker and Adamson Reagent grade absolute methanol "acetone-free." The vapor pressures of both samples were identical. The vapor pressure and infrared spectrum of the purified methanol were compared with that obtained simply by distillation over activated magnesium thru a 60 cm. laboratory column which was packed with glass helices and operated at about 5:1 reflux ratio. No difference either in spectrum or vapor pressure was observed; consequently, all subsequent samples were purified by the latter procedure. The methanol was allowed to reflux in the presence of magnesium turnings for a few hours and the first 15-25 ml of distillate were discarded. The boiling range of the product was $<0.1^{\circ}$ C. The observed boiling point corrected for pressure was 64.6° C.

Ethylene Chloride.

The ethylene chloride used in all of the experiments was either Matheson, Coleman and Bell (#5636) Pure Ethylene Chloride or Brothers Chemical Company (#1828) 1,2-dichloroethane. For the determination of the vapor pressure of the pure component, the manufactured product was twice distilled thru a highly efficient Todd laboratory column packed with glass helices and operated at 10:1 reflux ratio. In both distillations the first few milliliters were discarded and a fraction with a boiling range $<0.1^{\circ}$ C was retained. The vapor pressure and infrared spectrum of this product was compared with that obtained by a simple distillation thru a 60 cm heated column packed with glass helices. No difference was observed so the latter procedure was used for the subsequent preparation of all samples.

Carbon Tetrachloride.

Baker's Analyzed C. P. grade carbon tetrachloride was used throughout the study. It was purified before use by distillation thru a 30 cm column packed with glass helices. The column itself was equipped with an evacuated silvered jacket for insulation.

Carbon Disulfide.

Baker's Analyzed Reagent grade carbon disulfide was used after the following purification. The carbon disulfide was distilled from a mixture of mercury and mercurous sulfate thru a 60 cm column packed with amalgamated copper mesh. It was stored over mercury in brown bottles and kept away from sunlight. The product purified in this manner is completely free from the usual disagreeable odor associated with carbon disulfide. It has, in fact, a rather sweet, pleasant, ethereal odor. If stored as described above it will remain odor-free for several months.

Ether.

Mallinckrodt Anhydrous Ether was distilled over sodium metal and used immediately. Distillation was by means of a 100 cm Todd laboratory column packed with glass helices operated at 10:1 reflux ratio.

Chloroform.

Mallinckrodt Analytical Reagent grade chloroform was distilled thru a 100 cm glass helices-filled column operated at 10:1 reflux ratio.

Cobalt Chloride.

Eimer and Amend Reagent $CoCl_2 \cdot 6H_2O$ (with 0.2% Ni) was dissolved in concentrated hydrochloric acid and evaporated under vacuum to remove all the liquid. The resulting crystals were vacuum dried at 150° C for at least 24 hours. The resulting anhydrous "cake" was finely pulverized with a mortar and pestle. Since the grinding was done in the open the resulting fine powder was again heated to 150° C at a pressure less than 1.0 mm for about 12 hours. The resulting light blue anhydrous powder was stored in a rubber stoppered erlenmeyer flask inside of a desiccator until ready for use. The hydrochloric acid used in the preparation of the anhydrous salt was Baker's Reagent grade and was used without further purification.

CHAPTER III

THEORETICAL CONSIDERATIONS

Determination of Activity

The Binary System.

For the binary system methanol - $CoCl_2$, assuming the methanol vapor behaves as a perfect gas, the Gibbs-Duhem equation can be written as,

$$n_1 / n_2 \, d \log p_1 = - d \log a_2 \qquad (22)$$

Using moalities instead of mole fractions one obtains

$$k / m_2 \, d \log p_1 = - d \log a_2 \qquad (23)$$

but from experimental data one can obtain an analytical function of the type

$$\log p_1 = A + Bm_2 + Cm_2^2 + Dm_2^3 + Em_2^4 \qquad (24)$$

Substituting (24) in (23) and integrating one arrives at the following equation.

$$kB \ln m_2 + 2Ck \; m_2 + \frac{3Dk \; m_2^2}{2} + \frac{4Ek \; m_2^3}{3} + K^* = - \log a_2 \qquad (25)$$

where:

$$k = \frac{1{,}000}{32.04} = 31.211$$

B,C,D,E have the same significance as in (24)

K^* is a constant to be determined.

Since this investigation furnishes no information about the behavior of $CoCl_2$ in extremely dilute solutions of methanol, one cannot use the properties of the infinitely dilute solution to define the reference state as is conventional with aqueous solutions of electrolytes for which solute activity data is available in dilute regions. Even granting that the limiting law of Debye-Hückel is applicable at extreme dilutions, the uncertainty in the degree of dissociation of $CoCl_2$ at, and below the lowest experimentally studied concentrations would not allow a reliable extrapolation to be made to the limiting law region. As a practical alternative the saturated solution was chosen as the (arbitrary) standard state. Since in the standard state the solute activity is by definition unity, the right hand side of Equation (25) becomes equal to zero and K^* can be evaluated. Once K^* has been evaluated, all other values of $\underline{a}_2$ can be obtained simply by summing up the terms in the left hand side of Equation (25). This in effect, of course, relates all activities of $CoCl_2$ in the binary solution to the activity of $CoCl_2$ in the saturated solution.

Relating the Ternary to the Binary System.

The activity of the $CoCl_2$ in the ternary solutions can be related to the activity of the $CoCl_2$ in the binary solution by virtue of the fact that the solid phase in equilibrium with both the binary and the ternary systems is the same i.e. $CoCl_2 \cdot 3\ MeOH$. In the binary system $CoCl_2$ - MeOH we have at saturation the following equilibrium.

$$3\ \text{MeOH} + CoCl_2\ \left(\substack{\text{Sat.}\\ \text{soln.}}\right) \rightleftharpoons CoCl_2 \cdot 3\ \text{MeOH}\ (s) \tag{26}$$

Since the system is at equilibrium $\Delta\bar{F} = 0$ and

$$3\bar{F}\ (\text{MeOH}) + \bar{F}\ (CoCl_2)\ \left(\substack{\text{Sat.}\\ \text{soln.}}\right) = \bar{F}\ (CoCl_2 \cdot 3\ \text{MeOH})\ \ (s) \tag{27}$$

Since by definition $\bar{F} = \bar{F}^{o} + RT \ln a$, substituting this relation into (27) one gets

$$\begin{aligned} &3\bar{F}^{o}(\text{MeOH}) + 3\ RT \ln a\ (\text{MeOH}) + \bar{F}^{o}\ (CoCl_2)\ (s) + RT \ln a \\ &(CoCl_2)\ \left(\substack{\text{sat.}\\ \text{soln.}}\right) = \bar{F}^{o}\ (CoCl_2 \cdot 3\ \text{MeOH})\ (s) + RT \ln a(CoCl_2 \cdot 3\ \text{MeOH}). \end{aligned} \tag{28}$$

But by definition

$$\bar{F}^{o}\ (\mathrm{CoCl_2 \cdot 3\ MeOH})\ (s) = \bar{F}^{o}\ (\mathrm{CoCl_2})\ (s) + 3\bar{F}^{o}\ (\mathrm{MeOH}) \qquad (29)$$

Substituting (29) into (28), dividing by RT and changing to common logarithms, one obtains

$$3 \log a_B\ (\mathrm{MeOH}) + \log a_B\ (\mathrm{Cocl_2})\ \binom{\text{sat.}}{\text{soln.}} = \log a(\mathrm{CoCl_2 \cdot 3\ MeOH}) \qquad (30)$$

In a similar fashion we derive for the ternary solution

$$3 \log a_T(\mathrm{MeOH}) + \log a_T(\mathrm{Cocl_2})\ \binom{\text{sat.}}{\text{soln.}} = \log a\ (\mathrm{CoCl_2 \cdot 3\ MeOH}) \qquad (31)$$

Subtraction of (30) from (31) leaves finally

$$\begin{aligned} \log a_T(\mathrm{CoCl_2})\binom{\text{sat.}}{\text{soln.}} &= 3 \log a_B(\mathrm{MeOH}) + \log a_B(\mathrm{CoCl_2})\binom{\text{sat.}}{\text{soln.}} \\ &\quad -3 \log a_T(\mathrm{MeOH}) \end{aligned} \qquad (32)$$

The subscripts T and B refer to that particular species in the ternary solution and the binary solution respectively.

The first and third terms in the right hand side of Equation (32) were evaluated from the vapor pressure data and the second term was arbitrarily set equal to zero since the saturated binary solution was chosen as the reference state. In this way the activity of $\mathrm{CoCl_2}$ in the saturated ternary solution was evaluated. To find the activity at any other concentration, however, it was necessary to integrate the Gibbs-Duhem equation for the ternary system. This was done as follows.

The Ternary System.

The Gibbs-Duhem equation for a ternary system can be written as

$$n_1\ d \ln a_1 + n_2\ d \ln a_2 + n_3\ d \ln a_3 = 0 \qquad (33)$$

Since $a_i = \frac{p_i}{p^o}$ for ideal gases and components 1 and 2 are vapors at low pressures, one may write

$$n_1 d \ln p_1 + n_2\ d \ln p_2 + n_3\ d \ln a_3 = 0 \qquad (34)$$

After dividing by 2.303 n_1 (34) becomes

$$d \log p_1 + \frac{n_2}{n_1} d \log p_2 + \frac{n_3}{n_1} d \log a_3 = 0 \tag{35}$$

If n_2/n_1 is kept constant (in this case $n_2/n_1 = k = 0.5$) (35) can be integrated to give

$$K \int \frac{d \log p_1}{m_3} + kK \int \frac{d \log p_2}{m_3} = - \int d \log a_3 \tag{36}$$

Here $K = \frac{1,000}{32.04}$ the number of moles of methanol per 1,000 grams. If analytical equations can be found which relate $\log p_1$ and $\log p_2$ to m_3 and have the form

$$\log p_1 = A + Bm_3 + Cm_3^2 + Dm_3^3 + Em_3^4 \tag{37}$$

and

$$\log p_2 = A' + B'm_3 + C'm_3^2 + D'm_3^3 + E'm_3^4 \tag{38}$$

then differentiation gives

$$d \log p_1 = (0 + B + 2Cm_3 + 3Dm_3^2 + 4Em_3^3)\ dm_3 \tag{39}$$

and

$$d \log p_2 = (0 + B' + 2C'm_3 + 3D'm_3^2 + 4E'm_3^3)\ dm_3 \tag{40}$$

Substituting (39) and (40) in (36) and integrating one has finally

$$\begin{aligned} -\log a_3 = {} & (KB+\bar{K}B')\ln m_3+2(KC+\bar{K}C')m_3+3/2(KD+\bar{K}D')m_3^2 \\ & +4/3(KE+\bar{K}E')m_3^3+C^* \end{aligned} \tag{41}$$

Here $\bar{K} = kK$ and C^* is the integration constant. The constant C^* can be determined by substituting into Equation (41) the value of a_3 in the saturated ternary solution, obtained from Equation (32). All subsequent values of $\underline{a}_3$, of course, are evaluated by summing up all the terms in the right hand side of (41). If all of the constants in each term in Equation (41) are combined, the equation reduces to one of the form

$$-\log a_3 = \alpha \ln m_3 + \beta m_3 + \gamma m_3^2 + \delta m_3^3 + C^* \quad . \tag{42}$$

Determination of p_1 and p_2 From Vapor Pressure and Spectral Data

In the following derivations p_i, n_i, N_i, M_i and g_i refer respectively to the partial pressure, number of moles, mole fraction, molecular weight and number of grams of the i^{th} component of the solution.

For a mixture of ideal gases or vapors it is known that

$$p_1 = N_1 P_t \tag{43}$$

but by definition

$$N_1 = n_1 / n_1 + n_2 \tag{44}$$

where also by definition

$$n_i = g_i / M_i \tag{45}$$

Substituting (45) into (44) gives

$$N_1 = \frac{g_1 / M_1}{g_2 / M_2 + g_1 / M_1} \tag{46}$$

which reduces to

$$N_1 = \frac{1}{1 + M_1 / M_2 \cdot g_2 / g_1} \tag{47}$$

Hence

$$p_1 = \frac{P_t}{1 + M_1 / M_2 \cdot g_2 / g_1} \tag{48}$$

and

$$p_2 = \frac{P_t}{1 + M_2 / M_1 \cdot g_1 / g_2} \tag{49}$$

If g_1 and g_2 are both dissolved in the same weight W of solvent then

$C_1 = g_1 / W$ and $C_2 = g_2 / W$, so $(g_1 / g_2) = (C_1 / C_2)$.

Making this substitution, Equations (48) and (49) become Equations (18) and (19) which were presented earlier without derivation. In this study methanol was component 1 and ethylene chloride was component 2 so that $M_1 / M_2 = 0.3237$ and $M_2 / M_1 = 3.089$

Hence

$$p_1 = \frac{P_t}{1+0.3237\ (C_2/C_1)} \quad \underline{\text{or}} \quad p_2 = \frac{P_t}{1+3.089\ (C_1/C_2)} \tag{50}$$

$\underline{P}_t$ was measured directly by the manometric apparatus. The pressures $\underline{p}_1$ and $\underline{p}_2$ were calculated from Equation (50) after the ratio (C_1/C_2) was determined from spectral data as follows.

Consider the spectrophotometric analysis of two components in a mixture. If the optical density ($\underline{D}$) varies with concentration in a linear fashion one can write down the following equations where the superscripts of $\underline{D}$ refer to wave length and the subscripts refer to the component in question.

$$D_T^1 = D_1^1 + D_2^1 \tag{51}$$

$$D_T^2 = D_1^2 + D_2^2 \tag{52}$$

where

$$D_1^1 = k_1\ C_1 + a;\ D_2^1 = k_2\ C_2 + b \tag{53}$$

and

$$D_1^2 = k_3\ C_1 + c;\ D_2^2 = k_4\ C_2 + d \tag{54}$$

If Beer's law holds strictly, the constants $\underline{a}, \underline{b}, \underline{c}, \underline{d}$ will all be equal to zero. However, in practice they usually have small positive values. Substituting (53) and (54) into (51) and (52) one obtains

$$D_T^1 = k_1\ C_1 + a + k_2\ C_2 + b \tag{55}$$

$$D_T^2 = k_3\ C_1 + c + k_4\ C_2 + d \tag{56}$$

Transposing the residuals gives

$$(D_T^1 - a - b) = k_1\ C_1 + k_2\ C_2 \tag{57}$$

$$(D_T^2 - c - d) = k_3\ C_1 + k_4\ C_2 \tag{58}$$

If one sets the left hand sides of Equations (57) and (58) equal to <u>A</u> and <u>B</u> respectively one has two equations in two unknowns

$$k_1 C_1 + k_2 C_2 = A \qquad (59)$$

$$k_3 C_1 + k_4 C_2 = B \qquad (60)$$

When (59) and (60) are solved simultaneously one obtains

$$C_2 = k_1 B - k_3 A / k_1 k_4 - k_2 k_3 \qquad (61)$$

and

$$C_1 = k_4 A - k_2 B / k_1 k_4 - k_2 k_3 \qquad (62)$$

If (62) is divided by (61) there results the final expression for (C_1 / C_2).

$$(C_1 / C_2) = k_4 A - k_2 B / k_1 B - k_3 A \qquad (63)$$

The various <u>k</u> values can be obtained by finding the slope of the best straight line relating concentration to optical density at the wave length chosen.

Thus, k_1 = slope of the D_1^1 vs. concentration curve

k_2 = slope of the D_2^1 vs. concentration curve

k_3 = slope of the D_1^2 vs. concentration curve

k_4 = slope of the D_2^2 vs. concentration curve

CHAPTER IV

DATA AND CALCULATIONS

Gas Phase Analysis

Methanol and Ethylene Chloride Alone.

The optical densities of ten samples of methanol vapor at pressures ranging from 0-92 mm were determined at a wavelength of 9.75 microns and the results are presented in Table I. The data are also shown in graphical form in Figure (5).

Thirteen samples of ethylene chloride at pressures from 0-70 mm were examined and the optical densities determined at a wave length of 8.07 microns. The data are presented numerically in Table I and graphically in Figure (6).

Methanol and Ethylene Chloride in Mixtures with Nitrogen at Constant $\underline{P}_t$

Optical densities of thirteen samples of ethylene chloride were measured at 8.07 microns. The partial pressure of the vapor was varied from 0-75 mm and the total pressure was kept at 122 mm by the addition of nitrogen.

Optical densities of eighteen samples of methanol were measured at 9.75 microns. The partial pressure of the methanol vapor was varied from 0-75 mm. The total pressure was kept at 122 mm by the addition of dry nitrogen. The data for both systems are presented numerically in

TABLE I

OPTICAL DENSITY OF METHANOL AND ETHYLENE CHLORIDE AT VARIOUS PARTIAL AND TOTAL PRESSURE

MeOH $P_1 = P_t$		$EtCl_2$ $P_1 = P_t$		$EtCl_2$ P_t = 122mm		MeOH P_t = 122mm		*MeOH, P_t = 122mm	
Press. mm Hg	O. D. λ =9.75μ	Press. mm Hg	O. D. λ =8.07μ	Press. mm Hg	O. D. λ =8.07μ	Press mm Hg	O. D. λ =9.75μ	Press. mm Hg	O. D. λ =9.75μ
92.0	0.940	67.8	1.071	73.4	1.258	75.6	0.833	120.0	1.221
81.2	0.890	59.5	0.955	64.9	1.167	71.7	0.809	117.9	1.219
72.0	0.761	52.3	0.843	57.8	1.042	70.1	0.791	116.6	1.196
67.3	0.695	49.3	0.803	53.6	0.984	68.9	0.772	115.4	1.200
50.2	0.542	43.6	0.733	44.7	0.807	67.3	0.749	114.4	1.171
41.5	0.445	35.9	0.618	39.3	0.712	65.2	0.735	112.2	1.163
30.1	0.333	32.8	0.584	35.6	0.650	62.7	0.720	106.9	1.125
22.9	0.246	28.7	0.503	33.2	0.620	60.5	0.699	99.9	1.070
9.9	0.109	20.8	0.387	28.3	0.524	58.7	0.689	91.7	0.991
9.6	0.129	17.4	0.332	23.3	0.408	55.8	0.660	89.8	0.978
		12.4	0.239	18.7	0.326	53.7	0.640	87.4	0.959
		7.5	0.145	11.5	0.225	46.6	0.541	82.7	0.912
		6.6	0.109	8.8	0.141	40.3	0.490	80.0	0.885
						32.2	0.398	77.8	0.869
						23.4	0.310	67.5	0.766
						16.1	0.215	65.4	0.737
						6.2	0.111	58.0	0.680
						3.0	0.049	47.4	0.570
								41.2	0.498
								32.6	0.403
								25.9	0.325
								22.4	0.294
								21.9	0.302
								18.1	0.232
								17.3	0.227
								10.8	0.158
								6.0	0.089
								2.7	0.040

*O.D. measurement made with potentiometer instead of Speedomax recorder

Figures 7 and 8.

Another series of twenty-eight samples of methanol at various partial pressures from 0-120 mm and a constant total pressure of 122 mm were examined. The optical densities were obtained at 9.75 microns by use of a manually operated potentiometer instead of a recording potentiometer. Graphical results are presented in Figure 9 and the numerical data are included in Table I.

Liquid Phase Analysis (Medium Infrared)

Methanol and Ethylene Chloride in Carbon Disulfide Solutions.

Optical densities of eleven solutions of methanol in carbon disulfide were determined. The wave length used for analysis was 10.2 microns and the cell was a 1 mm fixed-thickness liquid cell fitted with NaCl windows. The optical densities of nine solutions of ethylene chloride over approximately the same concentration range were also measured at 14.3 microns. The results of these determinations are presented numerically in Table II and graphically in Figures 10 and 11.

Liquid Phase Analysis (Near Infrared)

Methanol at 2510 and 1703 Millimicrons.

To test Beer's law and to obtain the values of $\underline{k}_1$, $\underline{k}_3$, $\underline{a}$, and $\underline{c}$ for use with Equations (53) and (54) a series of twenty solutions of methanol in carbon tetrachloride were analyzed and optical densities determined at wave lengths of 1703 and 2510 millimicrons. The results are given in Table III. The optical densities were plotted against concentrations on large sheets of graph paper approximately 2 ft. x 2 ft. The equation of the line was obtained by drawing the best straight

TABLE II

OPTICAL DENSITIES OF SOLUTIONS OF METHANOL AND ETHYLENE CHLORIDE IN CARBON DISULFIDE-MEDIUM INFRARED

Methanol		Ethylene Chloride	
$\frac{\text{gms}}{100\ \text{gms}\ CS_2}$	O. D. $\lambda = 10.2\mu$	$\frac{\text{gms}}{100\ \text{gms}\ CS_2}$	O. D. $\lambda = 14.3\mu$
0.357	1.150	0.348	0.640
0.345	0.111	0.278	0.517
0.296	0.992	0.264	0.498
0.182	0.685	0.247	0.478
0.163	0.625	0.201	0.396
0.146	0.564	0.156	0.313
0.121	0.484	0.129	0.260
0.108	0.433	0.095	0.197
0.091	0.375	0.053	0.111
0.060	0.253		
0.045	0.188		

TABLE III

OPTICAL DENSITY VS. CONCENTRATION FOR SOLUTIONS OF METHANOL AND ETHYLENE CHLORIDE IN CARBON TETRACHLORIDE AT 2510 AND 1703 MILLIMICRONS

Methanol			Ethylene Chloride		
Molality ($CoCl_2$)	O. D. λ =2510mu	O. D. λ =1703mu	Molality ($CoCl_2$)	O. D. λ =2510mu	O. D. λ =1703mu
0.2464	0.118	0.0137	0.4824	0.0179	0.0588
0.2934	0.137	0.0212	1.021	0.0366	0.121
0.4886	0.220	0.0314	1.519	0.0515	0.179
0.6218	0.274	0.0374	1.995	0.0689	0.233
0.7288	0.323	0.0453	2.496	0.0860	0.293
0.9311	0.403	0.0569	2.951	0.1007	0.347
0.9763	0.423	0.0607	3.197	0.112	0.377
1.085	0.464	0.0648	3.459	0.119	0.405
1.2193	0.526	0.0737	4.106	0.142	0.477
1.242	0.529	0.0759	4.936	0.169	0.572
1.400	0.598	0.0828			
1.470	0.633	0.0900			
1.569	0.671	0.0986			
1.757	0.752	0.110			
1.871	0.795	0.118			
1.890	0.804	0.122			
1.950	0.835	0.126			
2.079	0.892	0.135			
2.083	0.891	0.130			
2.253	0.968	0.141			

at 2510 millimicrons

$$D_1^1 = 0.4195\ C_1 + 0.0140$$

at 1730 millimicrons

$$D_1^2 = 0.623\ C_1 \pm 0.0000$$

$k_1 = 0.4195$ $a = 0.0140$

$k_3 = 0.0623$ $c = 0.0000$

at 2510 millimicrons

$$D_2^1 = 0.0341\ C_2 + 0.0015$$

at 1703 millimicrons

$$D_2^2 = 0.1173\ C_2 + 0.0010$$

$k_2 = 0.0341$ $b = 0.0015$

$k_4 = 0.1173$ $d = 0.0010$

line by eye thru the points. The *k* values were found from the slopes of the lines and the values of *a* and *c*, from the *y* (O. D.) intercepts.

Ethylene Chloride at 2510 and 1703 Millimicrons.

A series of the solutions of known concentration of ethylene chloride in carbon tetrachloride were also analyzed and the optical densities were determined at 2510 and 1703 millimicrons. The results are given in Table III. The equation for the O. D. as a function of concentration was obtained in the same manner as for methanol. The values of $\underline{k}_2$, $\underline{k}_4$, *b* and *d* were determined as mentioned above from the slopes and intercepts of the curves.

Substituting the values thus obtained into Equations (57) and (58) the concentration ratio in Equation (63) becomes,

$$(C_1/C_2) = \frac{0.1173(D_T^1-0.0155)-0.0341(D_T^2-0.0010)}{0.4195(D_T^2-0.0010)-0.0623(D_T^1-0.0155)} \qquad (64)$$

This equation was used in all subsequent calculations of methanol and ethylene chloride concentrations from the observed optical densities in the near infrared.

Binary System $CoCl_2$ - MeOH

Vapor Pressure of Solutions.

The vapor pressures of twenty binary solutions of $CoCl_2$ in methanol, varying in concentration from zero to saturation, were measured, and the results are given in Table IV and Figure 15. By means of an I. B. M. Model 650 electronic computer, the quartic equation which gave the best agreement with the data was found by the method of least squares. It is

$$\hat{p}_1 = 126.65-5.130m_2-0.5421m_2^2+0.1831m_2^3-0.04515m_2^4 \qquad (65)$$

Values of $\underline{p}_1$ computed from the equation are designated as $\hat{\underline{p}}_1$. The root

TABLE IV

OBSERVED AND COMPUTED VALUES OF p_1. CALCULATED VALUES OF a_1 AND a_2 FOR THE SYSTEM $CoCl_2$-MeOH

Molality ($CoCl_2$)	p (obs.)	p (comp.)	a_1 (MeOH)	Molality ($CoCl_2$)	a_2 ($CoCl_2$)
0.0000	126.6	126.65	1.000	0.2649	0.0161
0.2649	125.3	125.25	0.9889	0.4000	0.0281
0.2940	125.1	125.10	0.9877	0.6000	0.0495
0.3284	124.9	124.91	0.9863	0.8000	0.0749
0.3729	124.7	124.67	0.9843	1.000	0.1043
0.4330	124.4	124.34	0.9817	1.200	0.1378
0.4910	124.0	124.02	0.9792	1.400	0.1749
0.6403	123.2	123.18	0.9726	1.600	0.2180
0.8294	122.1	122.10	0.9641	1.800	0.2655
0.9226	121.4	121.56	0.9598	2.000	0.3190
1.083	120.7	120.63	0.9525	2.200	0.3796
1.434	118.5	118.53	0.9359	2.400	0.4488
1.649	117.1	117.20	0.9255	2.600	0.5281
1.860	116.0	115.87	0.9149	2.800	0.6200
2.134	114.2	114.08	0.9008	3.000	0.7280
2.540	111.1	111.24	0.8783	3.200	0.8857
2.840	108.8	108.96	0.8603	3.389*	1.000
2.882	108.8	108.62	0.8577		
3.174	106.2	106.18	0.8384		
3.389*	104.2	104.21	0.8228		

$$E(\text{r.m.s.}) = \sqrt{\frac{\sum (p_1 - \hat{p}_1)^2}{\sum p_1^2}} = 0.076\%$$

*Saturated Solution

mean square error between the observed pressure p_1 and the computed pressure $\hat{p}_1$, given by

$$E(\text{r.m.s.}) = \sqrt{\frac{\sum (p_1 - \hat{p}_1)^2}{\sum p_1^2}} \tag{66}$$

is also listed in Table IV.

Activities of MeOH and $CoCl_2$.

Since it was considered that the $\hat{p}_1$ values were probably more reliable than the p_1 values, the activities of methanol a_1, were calculated from the relation $a_1 = \dfrac{\hat{p}_1}{p_1^o}$.

In order to integrate the Gibbs-Duhem equation and thus obtain a_2, it was first necessary to obtain an analytical expression relating $\log p_1$ to m_2. Values of m_2 and the log of the corresponding p_1 value obtained from (65) were used to obtain the following equation, which was computed by the method of least squares.

$$\log p_1 = 2.10255 - 0.01732m_2 - 0.00254m_2^2 + 0.00075m_2^3 - 0.000196m_2^4 \tag{67}$$

After equating (67) and (24) to obtain the values of A, B, C, D, and E, these values were substituted in (25) to permit evaluation of a_2. The constant K* in (25) was determined by setting the right hand side of (25) equal to zero when m_2 was the concentration of $CoCl_2$ in MeOH at saturation. Values of a_2 were then calculated at equally spaced intervals (0.2 molal) of concentration. Both a_1 and a_2 are given in Table IV.

Vapor Pressure of the Solid Phases.

The vapor pressures of the three methanolates of $CoCl_2$ were measured at 25.00° and were found to be:

$$p\,(CoCl_2 \cdot 3\ MeOH) = 45.0\ mm$$

$$p\,(CoCl_2 \cdot 2\ MeOH) = 39.3\ mm$$

$$p\,(CoCl_2 \cdot MeOH) = 10.9\ mm$$

Lloyd (35) has obtained the following values for the vapor pressure of the tri-methanolate of $CoCl_2$.

At 20° $p\,(CoCl_2 \cdot 3\ MeOH) = 29.4$ mm

35° $p\,(CoCl_2 \cdot 3\ MeOH) = 81.9$ mm

Making the assumption that $\log p = k \frac{1}{T}$, interpolation of Lloyd's data yields the following value at 25°.

At 25° $p\,(CoCl_2 \cdot 3\ MeOH) = 42$ mm

This value is about midway between the values for the di-methanolate and the tri-methanolate obtained in this research. It is quite possible, that log p, however, is not a simple linear function of 1/T over the temperature range given. This could account for the slight discrepancy in values obtained.

Composition of the Solid Phase in the Ternary System

The solid phase in equilibrium with the ternary solution was shown to have the same composition as the solid in equilibrium with the binary solution by measurements of the following ratio.

$$\frac{\dfrac{(\text{Weight of Solid Phase})\ B}{(\text{Weight of } CoCl_2\text{-anhydrous})\ B}}{\dfrac{(\text{Weight of Solid Phase})\ T}{(\text{Weight of } CoCl_2\text{-anhydrous})\ T}}$$

The crystals were freed from most of their liquid phase by centrifuging them in a special tube with a fritted glass bottom. The final drying was done by pressing the crystals between several sheets of filter paper. Both samples were then dried at 150° C under vacuum to obtain anhydrous salt. Although some small amount of liquid may have adhered to the crystals even after the filter paper treatment, we can validly assume that approximately the same percentage of liquid adhered to both samples of solid phase. Thus, by using the ratio indicated above, any error in weight introduced by incomplete drying tends to cancel out. The average of three such ratios was found to be 0.983.

The Ternary System $CoCl_2$ - MeOH - $EtCl_2$

Vapor Pressures of the Mixtures.

The vapor pressures of fifteen ternary solutions containing various weights of $CoCl_2$ dissolved in methanol-ethylene chloride mixtures of constant mole ratio 2:1 were measured. The total pressures P_t, of the mixtures as a function of concentration are given in Table V and Figure 16. This data (P_t vs. molality) was used with the aid of the computer to find an analytical expression relating P_t to m_3. The quartic equation of best fit by the method of least squares was found to be,

$$\hat{P}_t = 158.7-2.881m_3+0.6448m_3^2-0.3407m_3^3+0.0285m_3^4 \qquad (68)$$

The computed values of $\hat{P}_t$ and the root mean square error, given by (66), are also listed in Table V. The latter is a measure of the fit of the equation to the data.

Ratio Analyses.

The equilibrium vapors from fifteen ternary solutions were frozen, dissolved in carbon tetrachloride and the optical density determined at 2510 and 1703 millimicrons. The ratio (C_1/C_2) was calculated from Equation (64). The concentrations m_3 (molality of $CoCl_2$ in methanol) and the corresponding ratios of (C_1/C_2) (designated as R) are tabulated in Table V and shown graphically in Figure (17). The quartic equation

TABLE V

CALCULATION OF p_1 AND p_2 FOR THE TERNARY SYSTEM MeOH - $CoCl_2$ - $EtCl_2$ MOLE RATIO OF $NeOH/EtCl_2$ IN LIQUID PHASE CONSTANT at 2.0

m_3 $CoCl_3$	O. D. (2510)	O. D. (1703)	R (obs.)	$\hat{R}$ (comp.)	m_3 $CoCl_2$	P_t (obs.)	$\hat{P}_t$ (comp.)	p_1	p_2
0.000	0.2940	0.1626	0.538	0.5383	0.000	158.7	158.7	99.1	59.6
0.3178	0.4188	0.2424	0.513	0.5136	0.3178	157.8	157.8	96.8	61.0
0.6202	0.3600	0.2132	0.491	0.4932	0.6202	157.1	157.1	94.8	62.3
1.032	0.3653	0.2220	0.472	0.4688	1.038	156.1	156.0	92.3	63.7
1.387	0.2760	0.1711	0.449	0.4496	1.387	155.1	155.1	91.0	64.1
1.649	0.2898	0.1836	0.436	0.4360	1.668	154.3	154.3	88.5	65.8
1.917	0.3608	0.2354	0.423	0.4224	1.894	153.5	153.6	87.1	66.5
2.167	0.3618	0.2416	0.409	0.4098	2.167	152.8	152.6	85.3	67.3
2.453	0.3591	0.2455	0.394	0.3957	2.453	151.5	151.5	83.3	68.2
2.722	0.3304	0.2291	0.383	0.3826	2.722	150.3	150.3	81.4	68.9
2.933	0.4224	0.3001	0.375	0.3727	2.933	149.3	149.3	79.9	69.4
3.147	0.3751	0.2721	0.361	0.3631	3.125	148.3	148.3	78.5	69.8
3.359	0.3619	0.2648	0.355	0.3543	3.359	147.0	147.0	76.8	70.2
3.455	0.3632	0.2672	0.352	0.3506	3.455	146.5	146.5	76.1	70.3
3.643	0.3981	0.2991	0.343	0.3440	3.643	145.3	145.3	74.9	70.4

E(r.m.s.) = 0.35%

E(r.m.s.) = 0.036%

which best fit this data by least squares method was found to be

$$\hat{R} = 0.5383-0.08463m_3+0.6448m_3^2-0.3407m_3^3+0.0285m_3^4 \quad (69)$$

The computed values of the ratio $\hat{\underline{R}}$ are given in Table V along with the R. M. S. error which is a measure of the fit of the equation to the data.

Calculation of $\underline{p}_1$ and $\underline{p}_2$ From $\hat{\underline{R}}$ and $\hat{\underline{P}}_t$.

It has been shown that $\underline{p}_1$ and $\underline{p}_2$ can be calculated from Equations (18) and (19) once $\underline{P}_t$ and $\underline{R}$ are known. Since the computed values of $\hat{\underline{R}}$ and $\hat{\underline{P}}_t$ were considered, on the average, more reliable than the observed values, they were used to calculate $\underline{p}_1$ and $\underline{p}_2$. The calculated values of the partial pressure at various molalities are listed in Table V.

Activity of $CoCl_2$ in the Ternary System

Analytical expressions relating log p_1 and log p_2 to the molality of $CoCl_2$ was found by the method of least squares. They are

$$\log p_1 = 1.9959-0.03406m_3+0.00929m_3^2-0.00469m_3^3+0.0006m_3^4 \quad (70)$$

$$\log p_2 = 1.77554+0.03405m_3-0.01086m_3^2+0.004306m_3^3-0.0006m_3^4 \quad (71)$$

These correspond to Equations (37) and (38) mentioned in an earlier section.

Equation (32) was solved to obtain a value for $\underline{a}(CoCl_2)$ in the saturated ternary solution relative to $\underline{a}(CoCl_2)$ in the saturated binary solution. This value having been determined, the constant $\underline{C}^*$ in Equation (41) was evaluated and all subsequent values of $\underline{a}_3$ were calculated from Equation (41). Values of $\underline{a}_3$ were calculated at 0.2 molal intervals of concentration over the range from the most dilute solution to saturation. The calculated values of $\underline{a}_3$ at various concentrations are given in Table VI.

TABLE VI

CALCULATED VALUES OF THE ACTIVITY OF $CoCl_2$ IN THE TERNARY SYSTEM MeOH - $CoCl_2$ - $EtCl_2$

Molality	a_3
0.3178	0.0813
0.4000	0.1045
0.6000	0.1617
0.8000	0.2206
1.000	0.2826
1.200	0.3500
1.400	0.4246
1.600	0.5095
1.800	0.6066
2.000	0.7190
2.200	0.8498
2.400	1.004
2.600	1.181
2.800	1.390
3.000	1.633
3.200	1.914
3.400	2.237
3.643	2.693

CHAPTER V

DISCUSSION OF RESULTS

The problem of accounting for the thermodynamic behavior of a solution is essentially one of developing theoretical expressions consistent with what is known concerning the properties of the components of the solution which will express the various properties of the solution as functions of concentration, temperature or other relevant variables. Before an attempt can be made toward formulating any expression to describe the properties of solutions of cobalt chloride in methanol and in methanol-ethylene chloride mixtures it is necessary to give a brief description of what is thought concerning the various species present in the solution and the type of interactions that can be expected as the concentration of the various components is changed.

On the basis of spectrophotometric studies, Katzin (27) has furnished evidence that the magenta color in dilute solutions of cobalt chloride in methanol is due to the hexacoordinated species $CoCl_2 \cdot 4$ MeOH, a d^2sp^3 octahedral complex. In more concentrated solutions an intensely colored blue entity is formed for which he proposes the formula $CoCl_2 \cdot 2$ MeOH, an sp^3 type tetrahedral complex. The evidence in support of this formula, however, is much less direct than that for the tetrasolvate. In concentrated solutions both the magenta and the blue species are in equilibrium with each other and may be very easily interconverted by a slight change in temperature. Evidence for strong binding of four ligands to cobalt chloride is provided by the calculations of Katzin (28) for the energy of binding of water in the hydrates of $CoCl_2$. He showed for example that the second pair of water molecules is held about 60% as strongly as the first and the binding of alcohols is almost equal to that of water. In view of this it appears likely, assuming that the assignment of the formula $CoCl_2 \cdot 2\ MeOH$ to the blue species is correct, that two additional methanol molecules must be held rather strongly to the tetrahedral complex by electrostatic attraction. The hexacoordinate condition is relatively unstable at room temperature and can be converted to the blue tetracoordinated species by a slight increase in temperature. Pauling's coordination theory accounts for this instability on the grounds that Co (II) has only seven electrons to distribute among the 3d, 4s and 4p orbitals, and with maximum pairing, has only five vacant orbitals to accommodate six groups.

If an organic compound with a fairly strong nucleophilic group is added to a magenta solution of cobalt chloride in methanol ($CoCl_2 \cdot 4\ MeOH$), it should be able to compete with methanol for a coordination position around the cobalt atom. It should also hydrogen bond to some extent with the methanol molecules and leave them less available for coordination with the cobalt atom. Since both of these effects tend to lessen the attractive forces between the $CoCl_2$ and methanol molecules they should thus tend to convert some of the $CoCl_2 \cdot 4\ MeOH$ to $CoCl_2 \cdot 2\ MeOH$. The conversion may be observed visually because of the difference in color of the two species. In qualitative support of this hypothesis a series of compounds was chosen in which the electronic displacement by inductive or mesomeric effects diminished in the order indicated.

$(Me)_2CO > Et_2O >$ t-BuOH $>$ n-BuOH $> EtCl_2 > CCl_4 >$ cyclohexane

The effectiveness in producing the blue species also followed this same order, indicating that, indeed, the methanol molecules in the hexacoordinated $CoCl_2 \cdot 4\ MeOH$ may be effectively removed from their coordination position by another molecule which exhibits moderately strong interaction with methanol, or with the cobalt atom.

The blue color observed in concentrated solutions of cobalt chloride in a variety of solvents including methanol and water has also been explained on the basis of complex-ion formation. From conductance studies Wormser (71) concluded that a $CoCl_3^-$ entity exists in alcoholic solutions of cobalt chloride. In electrophoresis experiments with aqueous cobalt chloride solutions, Donnan and Bassett (10) observed that a blue entity migrated toward the anode and they postulated that it was $CoCl_3^-$. Mellor (39) notes that the addition of a salt which has very little tendency to form chloro-complexes, e.g. calcium chloride, to a magenta cobalt chloride solution causes the solution to turn blue indicating that some chloro-complex of cobalt is formed. On the other hand if a salt like zinc chloride which has a strong tendency to form chloro-complexes is added to a blue solution of cobalt chloride, the solution turns magenta indicating that some chloro-complex of zinc is formed at the expense of the blue chloro-complex of cobalt.

Even in fairly dilute solutions of cobalt perchlorate and lithium chloride Katzin (27) observed a blue entity at a Cl:Co ratio of 3:1. He cites spectrophotometric evidence to indicate that this blue entity is indeed not the same as the tetrahedral $CoCl_2 \cdot 2\ MeOH$ which is also blue. It seems rather likely that both blue species exist together in concentrated solutions of cobalt chloride. After many years of investigation there is still no general agreement as to the basis of the color change from magenta to blue in solutions of cobalt chloride. To be sure there is strong and convincing evidence to support both the desolvation and complex-ion interpretations.

Even though no data are available on the partial pressures of ethylene chloride-methanol mixtures, Scatchard and co-workers (62) have studied rather extensively the systems ethanol-chloroform and methanol-carbon tetrachloride. If one can assume that ethylene chloride behaves analogously to the other halogenated alkanes, there is much to be inferred from these studies. Ethylene chloride-methanol mixtures, as well as the systems mentioned above, show extremely large positive deviations from Raoult's law and Henry's law as might be expected considering the nature of the attractive forces involved. Methanol-methanol interaction should be quite strong because of the great tendency for hydroxyl groups to hydrogen bond. When the methanol aggregates are broken by ethylene chloride, the escaping tendency of the methanol is increased because methanol-ethylene chloride interaction is less than the methanol-methanol interaction which exists in the pure liquid. One of the interesting and quite unexpected results that came from Scatchard's work was that the excess entropy of mixing for solutions of methanol and carbon tetrachloride was <u>negative</u> over the entire concentration range, and further, that in ethanol-chloroform mixtures the excess entropy of mixing was also negative in the ethanol-rich mixtures. Scatchard interprets this to mean that in solutions exhibiting negative excess entropies of mixing, interaction between the alcohol and the halogenated hydrocarbon gives aggregates, each of which contains <u>more</u> molecules of alcohol than does an aggregate without the halogenated hydrocarbon. The attractive forces in the larger aggregates must be weaker than those in the pure alcohol, however, because of the large positive deviations from ideality actually observed in these mixtures. Scatchard proposes that interaction of the alcohol oxygen with the hydrogen of the halogenated hydrocarbon takes place as well as interaction of the halogen with the alcohol hydrogen. This seems quite reasonable in view of the electronegativity and polarizability of the chlorine atom. It seems entirely reasonable to expect that the methanol-ethylene chloride system would behave in a manner similar to the other alcohol-halogenated hydrocarbon systems, and that large loosely bound aggregates of methanol and ethylene chloride would be formed in the methanol-rich mixtures studied in these experiments. It must be emphasized, however, that even though the excess entropy may be negative the alcohol molecules are probably much more loosely bound than in the pure state (as shown by the extremely large positive deviations from Raoult's law). To give an idea of the magnitude of the deviation from ideality found in the methanol-ethylene chloride system, consider that a 2:1 mixture of methanol and ethylene chloride should give a partial pressure for methanol of 75.6 mm of Hg if the solution behaved ideally whereas the partial pressure actually observed was 99.1 mm of Hg.

The interaction between cobalt chloride and ethylene chloride may be assumed to be quite small because the solubility of the anhydrous salt in ethylene chloride was not measurable.

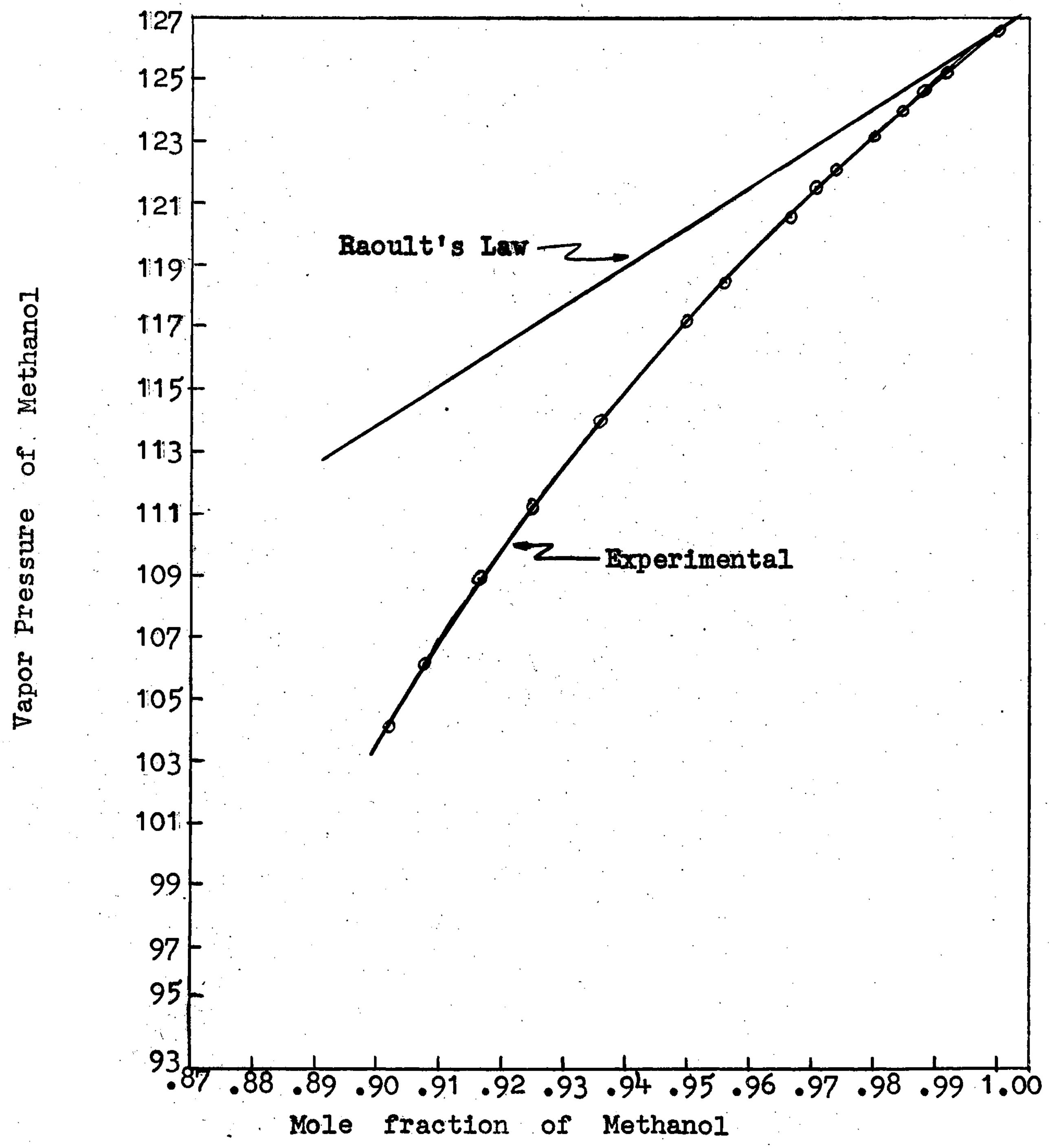
The Binary System, Cobalt Chloride - Methanol

Figure 18 shows p_1 the partial pressure of methanol as a function of N_1 its mole fraction in the solution. If Raoult's law were obeyed over the concentration range measured, p_1 would be given by the following equation.

$$p_1 = p_0 N_1$$

Figure 18

Negative Deviations from Raoult's Law for Methanol in the Binary Solution



The straight line which represents this equation is also shown in Figure 18. It was observed that the methanol vapor pressure shows rather large negative deviations from Raoult's law in solutions of cobalt chloride. The negative deviations were interpreted to mean that the methanol-cobalt chloride interaction was greater than the methanol-methanol interaction in the pure liquid, and consequently the salt must be rather extensively solvated in solution. This is in accordance with Katzin's observation mentioned earlier, that in dilute solutions four methanol molecules are attached to every molecule of cobalt chloride by coordination, and possibly several more are less strongly bound in the second solvation sphere.

When the solute-solvent interaction is sufficiently strong, Poynting (54) assumed that each solute molecule effectively removes several molecules of the solvent from the role of "free" solvent and thereby decreases the solvent vapor pressure in solution. Stokes and Robinson have used essentially the same model in successfully accounting for the effect of hydration in increasing the activity coefficients of aqueous solutions of electrolytes (59).

In line with Poynting's theory, it was assumed that methanol would follow Raoult's law if the effective mole fractions were used in place of the stoichiometric mole fractions. The effective mole fraction is written as

$$N_1^{\star} = n_1 - sn_2/n_1 + (1-s)n_2 \qquad (72)$$

in terms of the moles of solvent $\underline{n}_1$ and solute $\underline{n}_2$ and the solvation number $\underline{s}$ Written in terms of the respective stoichiometric mole fractions it is

$$N_1^{\star} = N_1 - N_2 s/1-N_2 s \qquad (73)$$

In order to test the usefulness of the Poynting theory, $\underline{a}_1$ was substituted for $\underline{N}_1^*$ and Equation (72) was rearranged to give

$$n_1 - a_1 (n_1 + n_2) = s \left[n_2 (1 - a_1) \right] \tag{74}$$

or using the more convenient molality notation we have

$$31.21 - a_1 (31.21 + m_2) = s \left[m_2 \ (1 - a_1) \right] \tag{75}$$

which is of the form $y = sx + b$. A plot of $\underline{Y}$ vs. $\underline{x}$ is shown in Figure 19. The linear portion (from $N_2 = 0.1$ to $N_2 = 0.03$) has a slope of $s \simeq 4$ in agreement with the formulation of a tetrasolvate. The fact that the linear segment does not extend to $N_2 = 0$ probably has its explanation in the fact that at low concentrations the cobalt chloride complex dissociates as a weak electrolyte. If one attempts to calculate the solvent vapor pressures from the assumption that Raoult's law holds for the undissociated tetrasolvate, he finds that the experimental points fall on a curve which parallels the calculated vapor pressure curve but which lies about 1.5 mm below it. This is shown in Figure 20. For reference is shown also the Raoult's law line disregarding solvation.

However, if the assumption is made that the tetrasolvate dissociates as a 1:1 electrolyte and that the ions formed are in equilibrium with the tetrasolvate, then the calculated values of the vapor pressure agree with the observed values within experimental error.

Consider the equilibrium between the tetrasolvate $CoCl_2 \cdot 4\,MeOH$ and the dissociation products $Co(4MeOH)Cl^+$ and Cl^-

$$CoCl_2 \cdot 4\,MeOH \rightleftharpoons Co(4MeOH)Cl^+ + Cl^-$$

If one mole of $CoCl_2 \cdot 4\,MeOH$ dissociates into x moles of $Co(4MeOH)Cl^+$ and x moles of Cl^-, then for any molality $\underline{m}$ of solute, the number of moles of the various species in solution will be:

Figure 19

Solvation Number of Solute

Test of Poynting's Theory

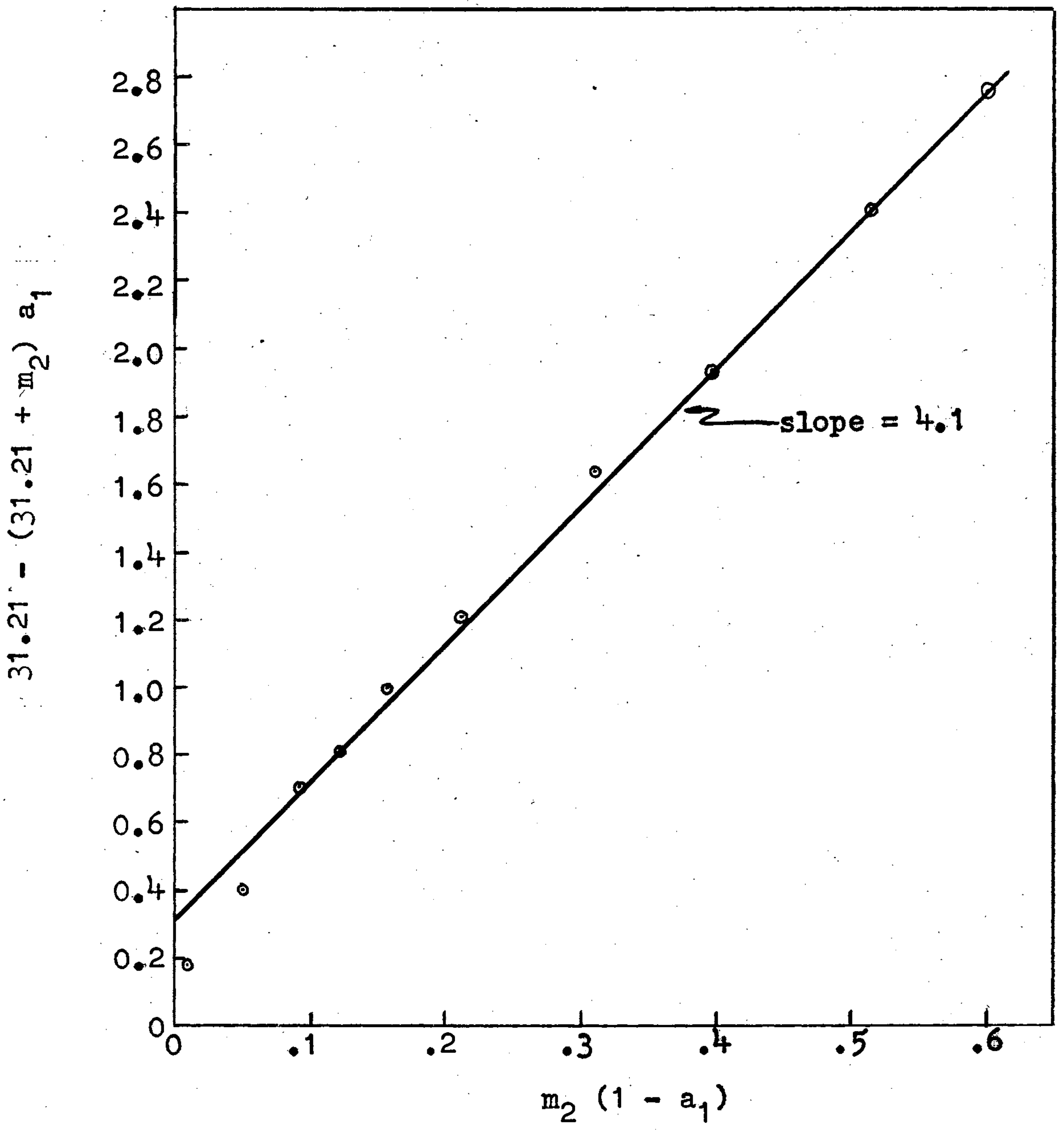
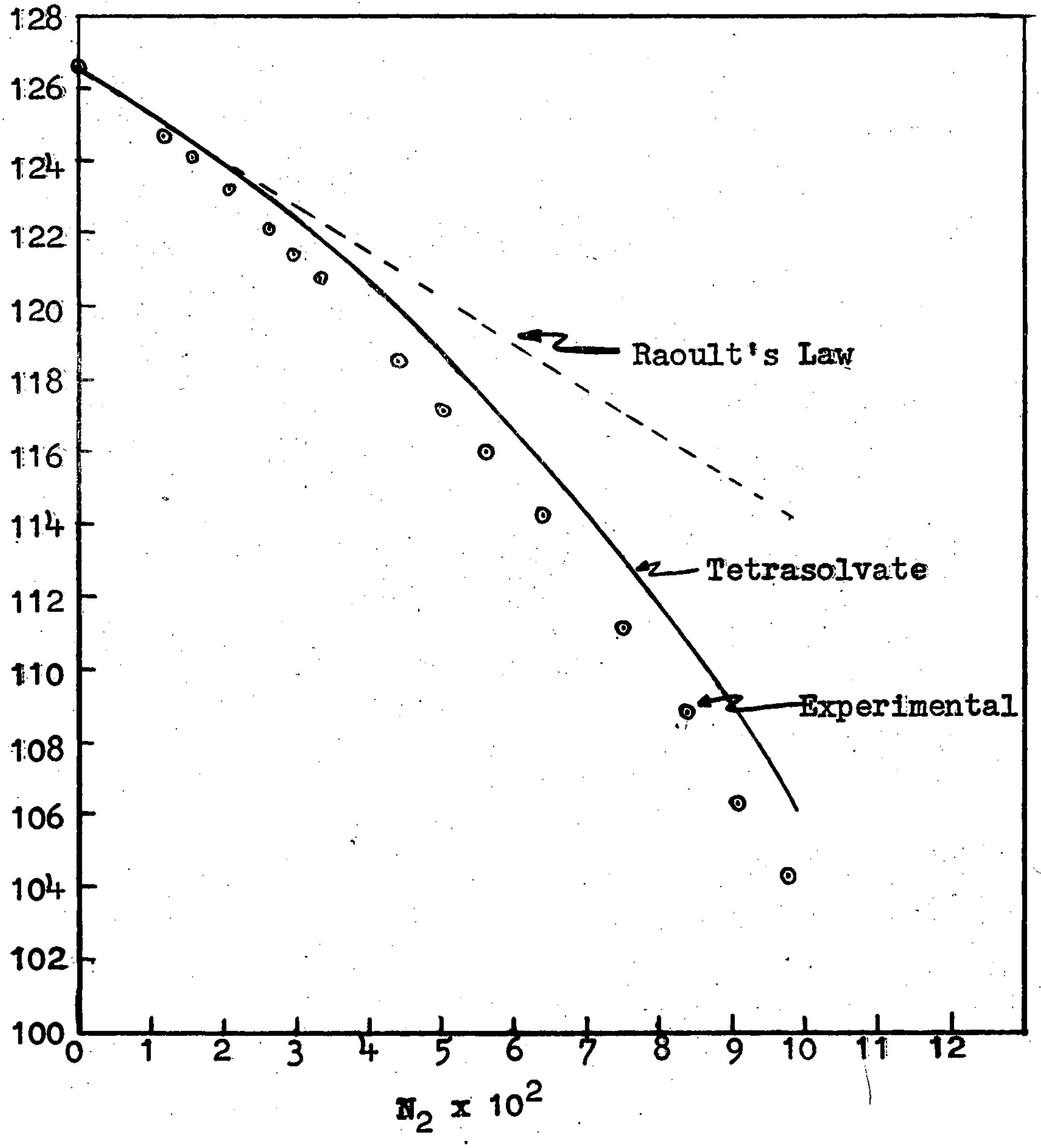


Figure 20

Calculated and Experimental Vapor Pressures of Methanol in Binary System MeOH - $CoCl_2$



$CoCl_2 \cdot 4\,MeOH$ = $m(1-x)$

$Co(4\,MeOH)Cl^+$ = mx

Cl^- = mx

MeOH (free) = $31.21 - 4m$

Total number of moles = $31.21 - 3m + mx$

Raoult's law for the vapor pressure of the "free solvent" is then written as

$$p_1 = N_1^{\star}\, p_1^{o} = \left[(31.21 - 4m)/(31.21 - 3m + mx)\right] p_1^{o} \qquad (76)$$

where mx, the concentration of the ionized species in the above equation, can be calculated from the following expression for the dissociation of the tetrasolvate.

$$K = \left[Co(4MeOH)Cl^+\right] \quad \left[Cl^-\right] \Big/ \left[CoCl_2 \cdot 4\,MeOH\right] \qquad (77)$$

Expressing concentrations as mole fractions we have

$$K = \frac{\left[\dfrac{mx}{31.21-3m+mx}\right]\left[\dfrac{mx}{31.21-3m+mx}\right]}{\left[\dfrac{m\,(1-x)}{31.21-3m+mx}\right]} \qquad (78)$$

which simplifies to

$$K = \frac{(mx)^2}{m(1-x)\;(31.21-3m+mx)} \qquad (79)$$

The quantity mx can be obtained from the above quadratic equation by the formula

$$mx = \frac{-\,K(31.21-4m) + \sqrt{K^2(31.21-4m)^2 + 4mK(1+K)(31.21-3m+[illegible])}}{2\,(1+K)} \qquad (80)$$

Substitution of (80) into (76) yields an equation in which the vapor pressure p_1 is a function of K, the dissociation constant of the tetrasolvate. If the value 2.7×10^{-3} is taken as the dissociation constant K, then Equation (76) will express p_1 the vapor pressure of methanol as a function of m_2, the molality of $CoCl_2$, well within experimental error of the actual observed values. Figure 21 shows the excellent agreement between the observed vapor pressure values and those calculated by Equation (76).

An alternative may also explain the dependence of $\underline{p}_1$ on $\underline{N}_1$ in the binary solution studied. Whereas the previous model assumed a constant solvation number, but partial ionization of the solute over the entire concentration range, this second model assumes that ionization of the solute occurs to a negligible extent over the concentration range studied, but allows for a variation in solvation number of the solute with concentration.

It is probably a gross oversimplification to represent the system as ideal even after account has been made for the effect of solvation, for Hildebrand and Scott (19), in their treatise on the solubility of nonelectrolytes, point out at least two other effects which may lead to deviations from Raoult's law in mixtures of nonelectrolytes. These are (1) non-zero heat of mixing and (2) non-zero entropy of mixing. In fact they have proposed that if a chemical treatment is to have any validity it must be superimposed not on Raoult's law, but upon a normal internal pressure treatment, assuming reasonable positive deviations from Raoult's law for the "true species."

Fowler and Guggenheim (14) have emphasized the difficulty in separating these effects except through their temperature dependence. However, in the absence of any experimental data from which to determine the magnitude of the deviations from ideality caused by the non-zero heat and entropy of mixing, all deviations from Raoult's law are thrown into the Poynting equation and the parameter s is computed for several experimental vapor pressures.

Figure 21

Experimental and Calculated Values for the Vapor Pressure of Methanol in the System $CoCl_2$ - MeOH Assuming Dissociation of the Tetrasolvate.

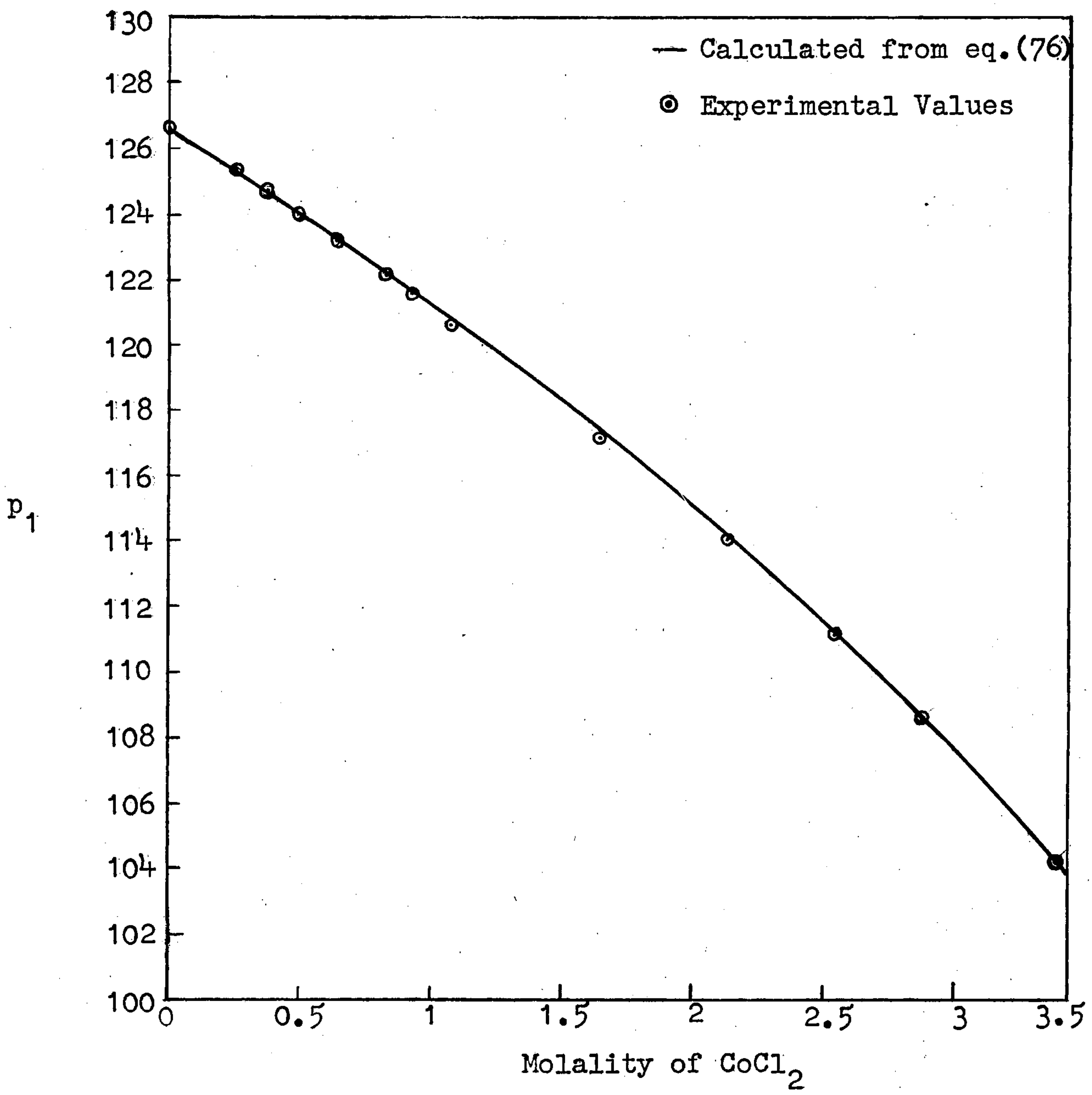


Figure 22 shows the dependence of $\underline{s}$ upon concentration thus calculated for the system studied. The general shape of the curve and the magnitude of the $\underline{s}$ values seem quite reasonable.

In dilute solutions the solvation number of nine could reasonably correspond to a $CoCl_2$ molecule with four coordinated methanol molecules and five methanol molecules in the second solvation sphere. All inter action past the second solvation sphere is considered small and therefore neglected. The solvation number of nine remains constant until nearly one quarter of the solvent molecules are combined. Robinson and Stokes (59) have shown that in actual practice, observed $\underline{s}$ values do remain essentially independent of concentration until about one quarter of the solvent molecules are combined. After this point is reached, $\underline{s}$ decreases in a more or less linear fashion with $\underline{N}_2$. At the higher concentrations near saturation another leveling off of the function is observed, for at high $\underline{N}_2$ values even a minute decrease in the average solvation number involves a partial desolvation of all the other solute molecules in solution. The solvation number near saturation of 4.78 is entirely reasonable in that some, though necessarily limited, interaction should be expected past the first solvation sphere which contains four coordinated methanol molecules.

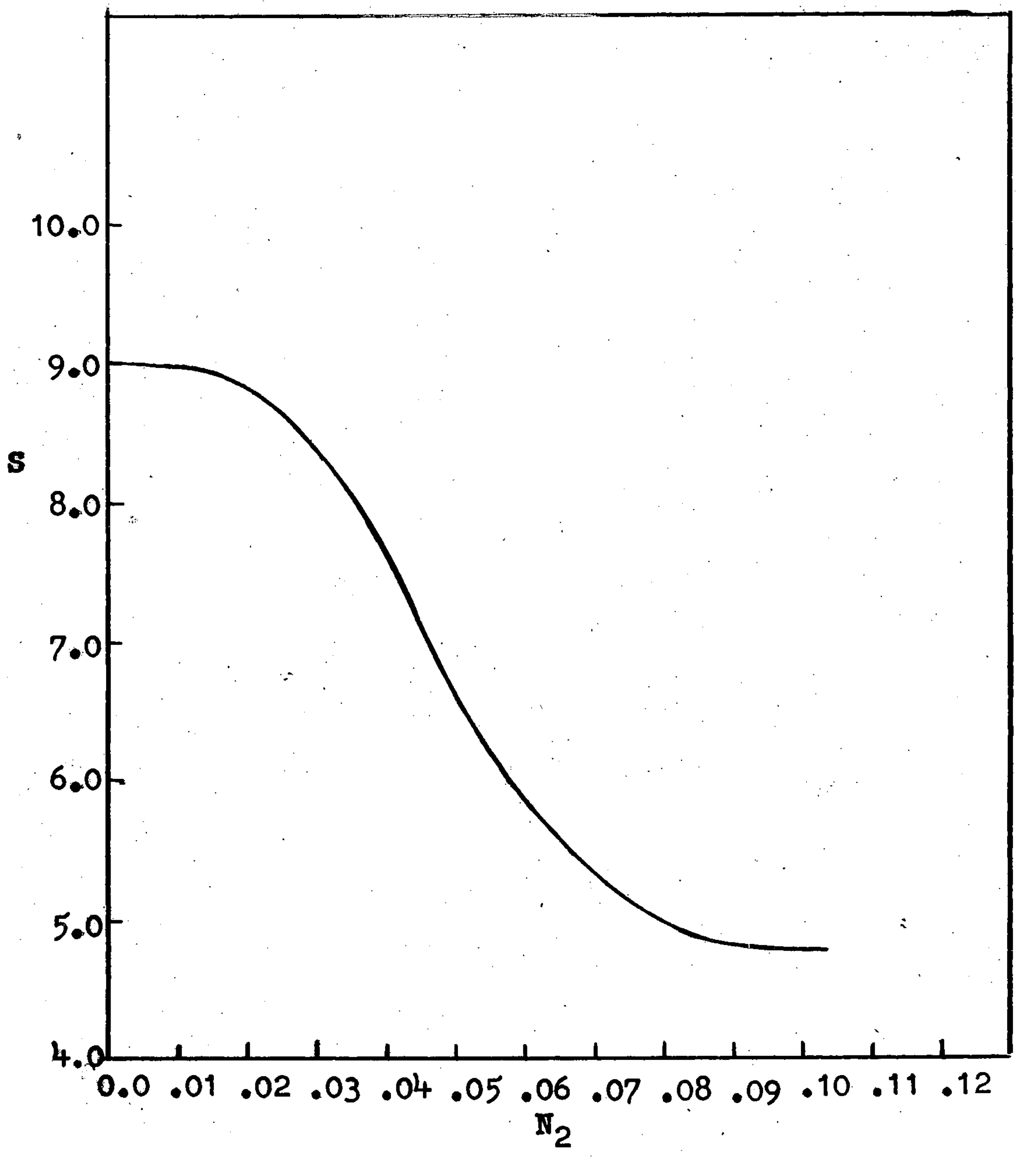
If numerical values of $\underline{s}$ taken from the curve in Figure 22 are substituted into the simple Poynting Equation (72), effective mole fraction values $\underline{N}_1^*$ are obtained which necessarily cause Raoult's law to reproduce the observed partial pressures of methanol.

In brief, two models have been proposed, both of which assume four solvent molecules in the first solvation sphere. The first model assumes that failure of the simple Poynting Equation (72) to account for the

Figure 22

Solvation Number of $CoCl_2$ as a

Function of Concentration (Mole Fraction)



concentration of "free solvent," assuming a tetrasolvate is due to dissociation of the tetrasolvate into a 1:1 electrolyte. The dissociation, of course, results in a greater number of solute particles in solution. Since vapor pressure is a colligative property and is dependent on the number of particles present in solution the net effect of the dissociation would be to lower the vapor pressure of the solvent below that caused by an undissociated tetrasolvate.

The other model, while not excluding the possibility of dissociation, essentially attributes the failure of Equation (72) to account for the concentration of "free solvent" to the ability of the solute molecule to exert its influence past the first solvation sphere and effectively "tie up" solvent molecules in the second solvation sphere.

Although one cannot be absolutely certain of the correctness of either proposed model, the dissociated tetrasolvate model is probably preferable to the latter one in which a variable solvation number is used, the value of <u>s</u> being determined as reasonable or empirically from the data.

Although the proposed models do not specifically support Katzin's characterization of the disolvate species, neither do they specifically testify against it. Katzin's conclusions were based on spectrophotometric studies of the various colored species in solution. The observed color changes are the result of gross peturbations in the electronic environment of the cobalt atom, but are not necessarily related to the actual solvation number of a particular species.

It is not at all unlikely, as pointed out earlier, that even assuming Katzin's characterization of the blue species as $CoCl_2 \cdot 2\ MeOH$ is correct, two additional methanol molecules could be held rather strongly to the tetrahedral complex by fairly strong electrostatic attraction.

From the vapor pressure data alone it is quite difficult to infer anything concerning the existence of the $CoCl_3^-$ species as proposed by others because the dissociation $2CoCl_2 \rightarrow CoCl^+ + CoCl_3^-$ does not represent an increase in the number of particles present and hence should not affect the colligative properties of the solution.

In view of Donnan's, Bassett's, and Wormser's evidence for the existence of a $CoCl_3^-$ ion even in concentrated solutions, it is reasonable to expect that at least a small degree of dissociation should be observed in dilute solutions. This is in accord with the dissociated tetrasolvate model proposed earlier.

Since Katzin had proposed, on the basis of spectrophotometric studies, that in fairly dilute solutions cobalt chloride exists as the undissociated entity $CoCl_2$, and our model allows only slight dissociation even in dilute solutions, it was expected that the salt would behave essentially as a nonelectrolyte over most of the concentration range. For many solutions of nonelectrolytes it is observed that ln f_2 is a linear function of $\underline{N}_2$. Robinson and Stokes (59) have presented the following explanation which is reproduced here. Starting with the Gibbs-Duhem equation for a binary solution of a nonelectrolyte one has

$$N_1 \frac{d\bar{G}_1}{dN_2} = - N_2 \frac{d\bar{G}_2}{dN_2} \tag{81}$$

Introducing activity coefficients it can be shown that

$$\left[\frac{d \ln f_1}{dN_2}\right] \Big/ \left[\frac{d \ln f_2}{dN_2}\right] = \frac{N_2}{1 - N_2} \tag{82}$$

It is clear that as $N_2 \rightarrow 0$, either of two things must happen

$$\frac{d \ln f_1}{dN_2} \rightarrow 0 \tag{83}$$

or

$$\frac{d \ln f_2}{dN_2} \longrightarrow -\infty \tag{84}$$

Guggenheim (16) points out that statistical theory requires that long-range forces must operate if the second alternative is to occur. But nonelectrolytes are characterized by short-range forces between solute particles and consequently the first alternative must apply. If this is so then

$$\frac{d \ln f_2}{dN_2} \longrightarrow \text{a constant as } N_2 \rightarrow 0.$$

If $\ln f_2$ is expressed as a power series in $\underline{N_2}$, the first term must contain $\underline{N_2}$ to the first power

$$\ln f_2 = AN_2 + BN_2^2 \ldots\ldots\ldots \tag{85}$$

In Equation (85) $\underline{f_2}$ is the activity coefficient obtained by choosing the ideal 1 molal solution as the standard state. If the saturated solution is chosen as the reference state, as in this work, then one obtains

$$\ln f_2\,(s) = AN_2 + BN_2^2 \ldots\ldots\ldots + \ln K \tag{86}$$

where ln K is defined by the equation

$$\ln K = \ln \frac{f_2(s)}{f_2^{\circ}} \tag{87}$$

Hence in dilute solutions of nonelectrolytes a plot of $\ln f_2\,(s)$ vs N_2 should produce a straight line of slope $\underline{A}$. Although the power series indicates that for large values of $\underline{N_2}$ deviations from linearity may occur, nevertheless, it is found in practice that for many nonelectrolytes $\ln f_2$ is linear with $\underline{N_2}$ up to mole fractions in the neighborhood of $N_2 = 0.08 - 0.09$ (65). This is about the concentration of cobalt chloride in very concentrated solutions in methanol. If, however, in the very dilute region around $N_2=0.01$ the solute ionizes to a certain extent, then long-range electrostatic attractions and repulsions would be found and as mentioned earlier, Equation (84) would hold and a slope of negative infinity would be obtained in very dilute solutions.

Figure 23 shows ln f_2 plotted against $\underline{N}_2$ the mole fraction of the solute in the binary solution. Ln f_2 was linear with $\underline{N}_2$ from the saturated solution to $N_2 = 0.02$ which supports the assumption made earlier that $CoCl_2$ exists primarily as the undissociated molecule in moderately dilute solutions. In the dilute region around $N_2 = 0.01$ the experimental points deviated from linearity and the curve began to assume the shape typical of electrolytes. Our data do not give the required negative infinite slope because measurements were not made at sufficiently low values of $\underline{N}_2$. Even in aqueous solutions of strong electrolytes the curves of activity coefficient vs. concentration do not show large negative slopes until the very dilute regions are reached. It should also be strongly emphasized, however, that accurate determinations of the solute activity in dilute regions by integration of the Gibbs-Duhem equation is extremely difficult (69), and too much significance should not be placed upon the shape of the curve in this region.

Since ln f_2 was found to be linear with N_2 over most of the concentration range studied, Equation (86) can be written

$$\ln f_2\ (s) = 16.5\ N_2 + 0.675 \qquad (88)$$

This equation suffices to express ln f_2 as a function of $\underline{N}_2$ over most of the concentration range with an error of about ± 1.0%. Since

$$a_2 = f_2\ (s)\ N_2 \qquad (89)$$

and

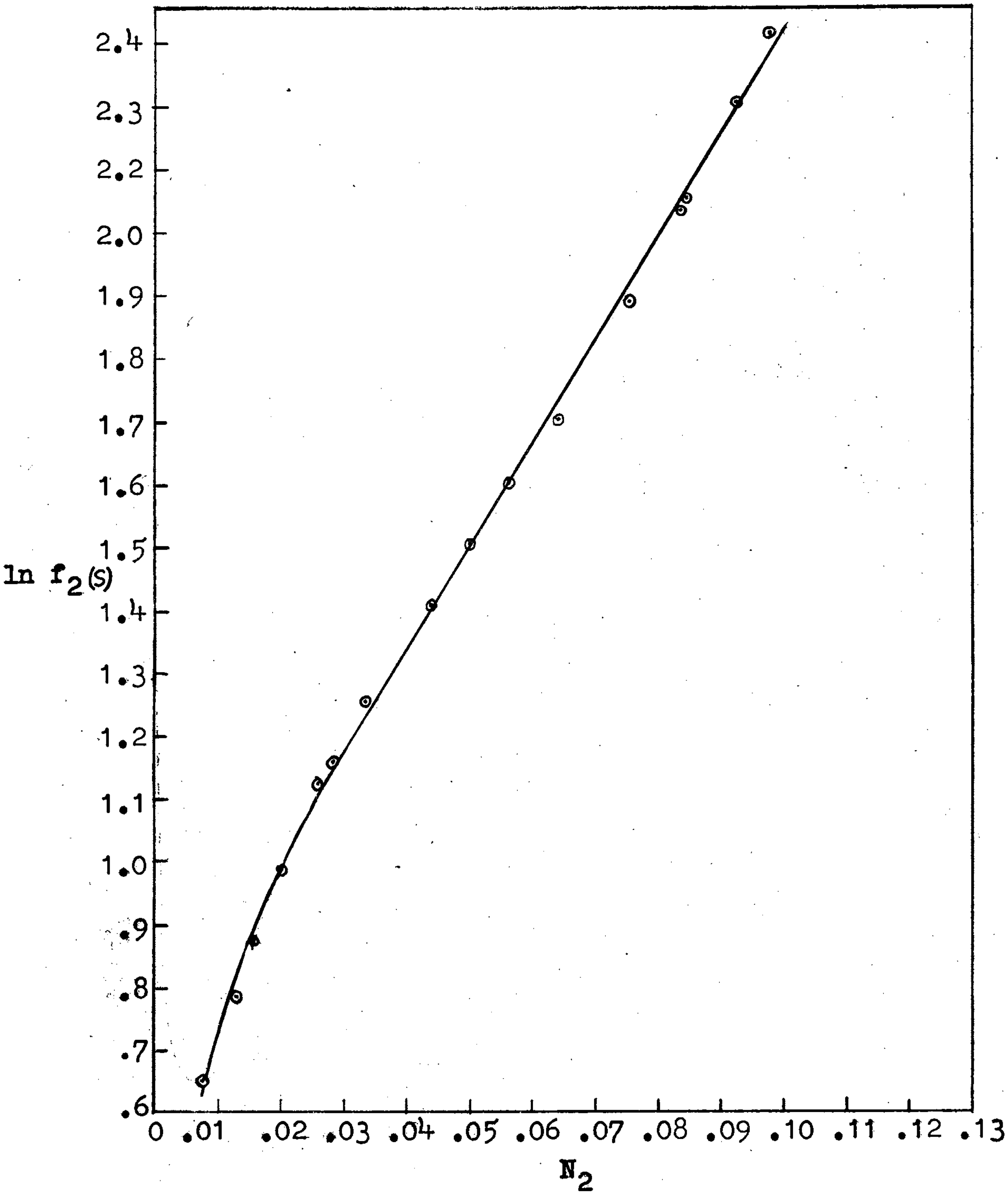
$$f_2\ (s) = e^{(16.5N_2 + 0.675)} \qquad (90)$$

then the activity of solutions of cobalt chloride in methanol, using the

Figure 23

$\ln f_2$ (Rational Activity Coefficient) vs

Mole Fraction $CoCl_2$ in Binary Solution



saturated solution as the reference state can be accurately expressed by

$$a_2 = N_2\, e^{(16.5\, N_2 + 0.675)} \qquad (91)$$

The Ternary System

Cobalt Chloride - Methanol - Ethylene Chloride

The variation in the thermodynamic properties of the components of the ternary mixture as a function of concentration are considerably more difficult to interpret than are the variations in the corresponding properties of the components of the binary system. Reference to Scatchard's work (61,62) on mixtures of alcohols and halogenated hydrocarbons shows that mixtures of such compounds show large positive deviations from Raoult's law, and that over certain concentration ranges, an extremely small change in the concentration of either component makes a considerable change in the partial pressure of both components. At other concentrations, however, the reverse is quite true.

At the present time there appears to be no really satisfactory theory of strong orientational effects from which one may deduce the thermodynamical properties of the solution from the properties of the pure components. Because of hydrogen bonding, liquids such as methanol are doubtless associated, and the influence of another liquid component is almost impossible to predict. In fact, investigations of the same system by different techniques have often resulted in conclusions quite in variance with each other. For example, in the system methanol-carbon tetrachloride, the ratio of methanol monomer to the total alcohol concentration has been measured by infrared spectroscopy and for dilute solutions of methanol in carbon tetrachloride was found to be in excellent agreement with that calculated from thermodynamic data, assuming a chemical equilibrium between the monomer and polymer species of methanol, but no complexes being formed between the methanol and carbon tetrachloride (55). On the other hand Scatchard et al (61, 62) have calculated the entropy of mixing of these two liquids and found it to be negative over the entire concentration range. They concluded that methanol must form aggregates with carbon tetrachloride even in dilute solutions. Although this is not the identical system studied in this work, it is anologous and emphasizes the difficulty involved in arriving at even a qualitative description of the alcohol-halogenated hydrocarbon system.

Addition of anhydrous cobalt chloride to such a mixture would be expected to change the effective mole ratio of the two liquids owing to solvation of the salt by one of the liquids only. The change in effective mole ratio would cause the vapor pressures of the two liquid components to vary in a manner very difficult to predict. The following is an attempt, however, to account for, at least in a qualitative fashion, the behavior of the various components as a function of salt concentration.

One might predict that the effect of introducing cobalt chloride into a mixture of ethylene chloride and methanol would be to increase the effective mole fraction of the ethylene chloride and to decrease the effective mole fraction (and thus the vapor pressure) of the alcohol through solvation of the cobalt chloride by the stronger base methanol. That this is in qualitative agreement with observation is shown by the curves in Figures 24 and 25.

Figure 24 shows an increase in the vapor pressure of ethylene chloride with an increase in the concentration of solute $CoCl_2$. Although it

Figure 24

Partial Pressure of $EtCl_2$ in Equilibrium Vapor

Ternary System $EtCl_2$ - MeOH - $CoCl_2$

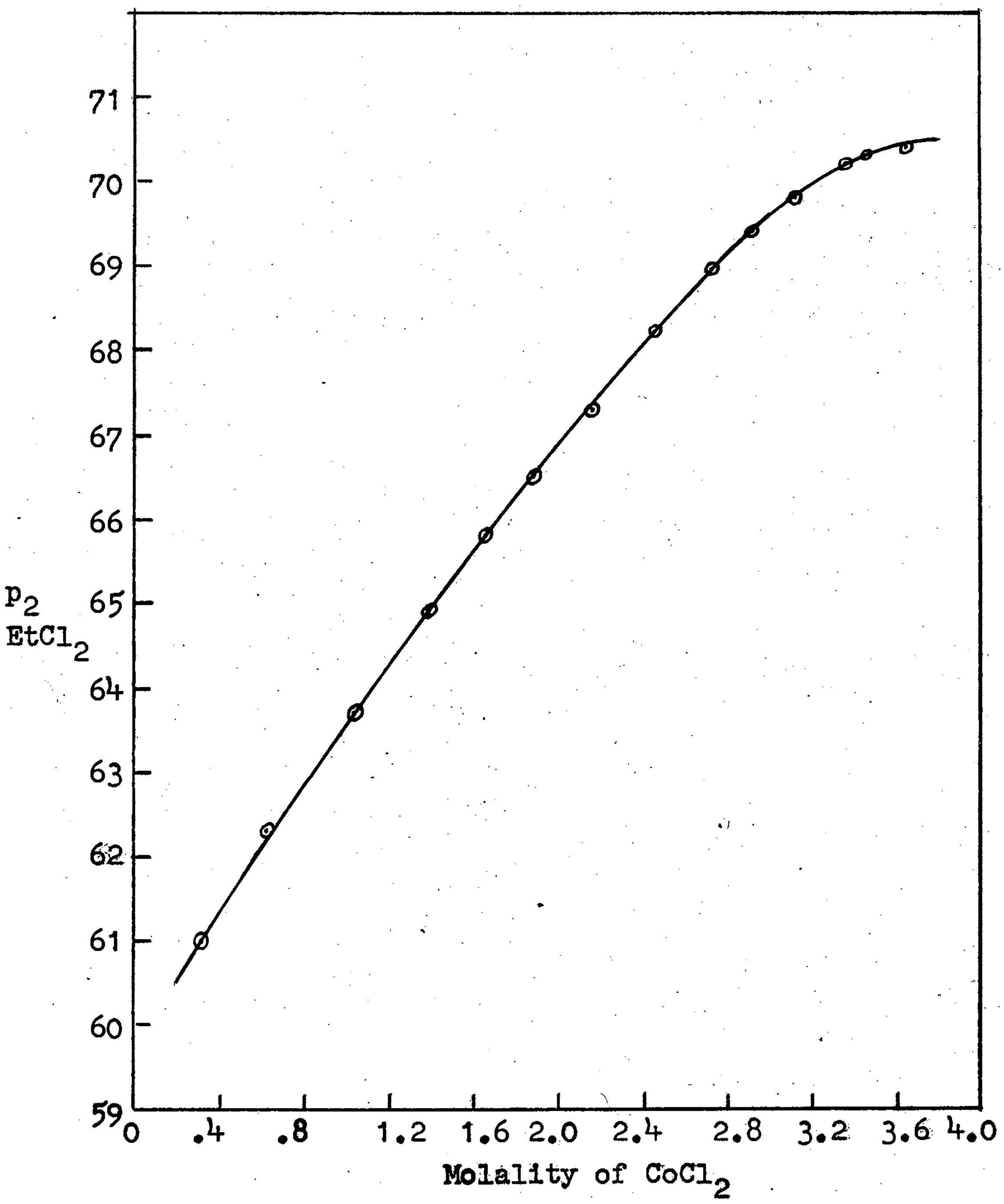
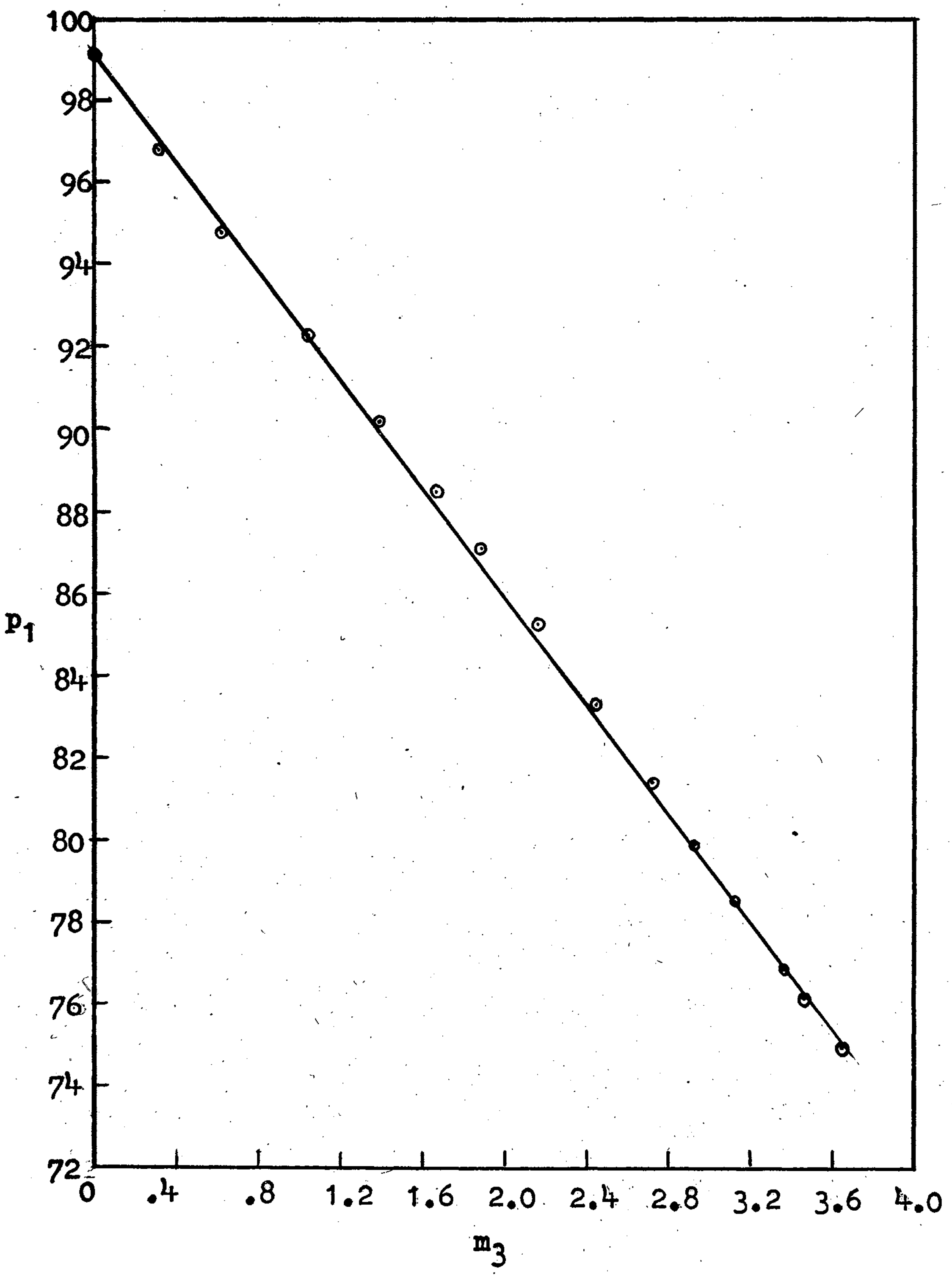


Figure 25

Partial Pressure of Methanol in the

Equilibrium Vapor of the

Ternary System $CoCl_2$ - MeOH - $EtCl_2$



is inconceivable that such a condition could exist in a binary solution, it is easily explained in the ternary solution. The factor which causes the increase in $\underline{p}_2$ with an increase in $\underline{m}_3$ (and consequently a decrease in mole fraction $\underline{N}_2$) is the solvation of the solute with methanol, but not with ethylene chloride. This solvation effectively removes methanol from the role of a solvent and leaves it unavailable to "tie up" ethylene chloride molecules in complexes or aggregates. One may envision the situation thus. Every methanol molecule which becomes associated with the added $CoCl_2$, frees several ethylene chloride molecules which it previously held in a weakly bound aggregate.

The stoichiometric mole fraction of ethylene chloride in the ternary solution is, of course, given by the defining equation.

$$N_2 = \frac{n_2}{n_1 + n_2 + n_3} \tag{92}$$

But if every cobalt chloride molecule is solvated with $\underline{s}$ molecules of methanol, then the effective mole fraction of ethylene chloride would be expressed by

$$N_2^* = \frac{n_2}{(n_1 - sn_3)+n_2+n_3} \tag{93}$$

From this we see that if $\underline{s}$ is greater than unity the effective mole fraction $\underline{N}_2^*$ and hence the partial pressure $\underline{p}_2$, increases as the molality of the solute $\underline{m}_3$ increases.

From Figure 24 one observes that at a cobalt chloride molality of about 3.2 a flattening out of the curve occurs, i.e., $\underline{p}_2$ increases less rapidly with increasing $\underline{m}_3$. Examination of Equation (93) shows that a decrease in $\underline{s}$ at high concentrations would cause $\underline{N}_2^*$, and presumably $\underline{p}_2$, to become more nearly constant as $\underline{m}_3$ increases. This decrease in solvation number in nearly saturated solutions is certainly to be expected and is in accord with the solvation model proposed earlier for the binary solution.

Figure 25 shows the expected decrease in partial pressure p_1 of methanol with increasing solute concentration. As with the binary solution, the decrease in partial pressure is due primarily to the solvation of the $CoCl_2$ with the methanol and the resultant decrease in concentration of "free" methanol. The decrease in partial pressure is a linear function of the concentration of solute and is given within experimental error by the equation.

$$p_1 = 99.1 - 6.611 \, m_3 \tag{94}$$

Comparison of Figures 15 and 25 reveals some interesting points. The saturated binary solution contains 3.39 moles of cobalt chloride per 1,000 grams of methanol, while the saturated ternary solution contains 9.26 moles of cobalt chloride per 1,000 grams of methanol. Even though ethylene chloride alone does not dissolve cobalt chloride, it greatly enhances the ability of methanol to do so. One may conjecture that the reason for this behavior is due, at least partly, to the fact that ethylene chloride breaks up the strongly bound methanol aggregates and forms weakly bound methanol-ethylene chloride aggregates, similar to the situation proposed by Scatchard. The free energy for the solution of cobalt chloride in methanol can be considered to consist essentially of two parts: 1) the free energy of depolymerization of methanol aggregates and: 2) the free energy of solvation of the salt. Since the former process requires the expenditure, rather than the release of energy it is obvious that any condition which will reduce the energy required to depolymerize the methanol aggregates will increase the solubility of the salt. This is precisely the behavior reported by

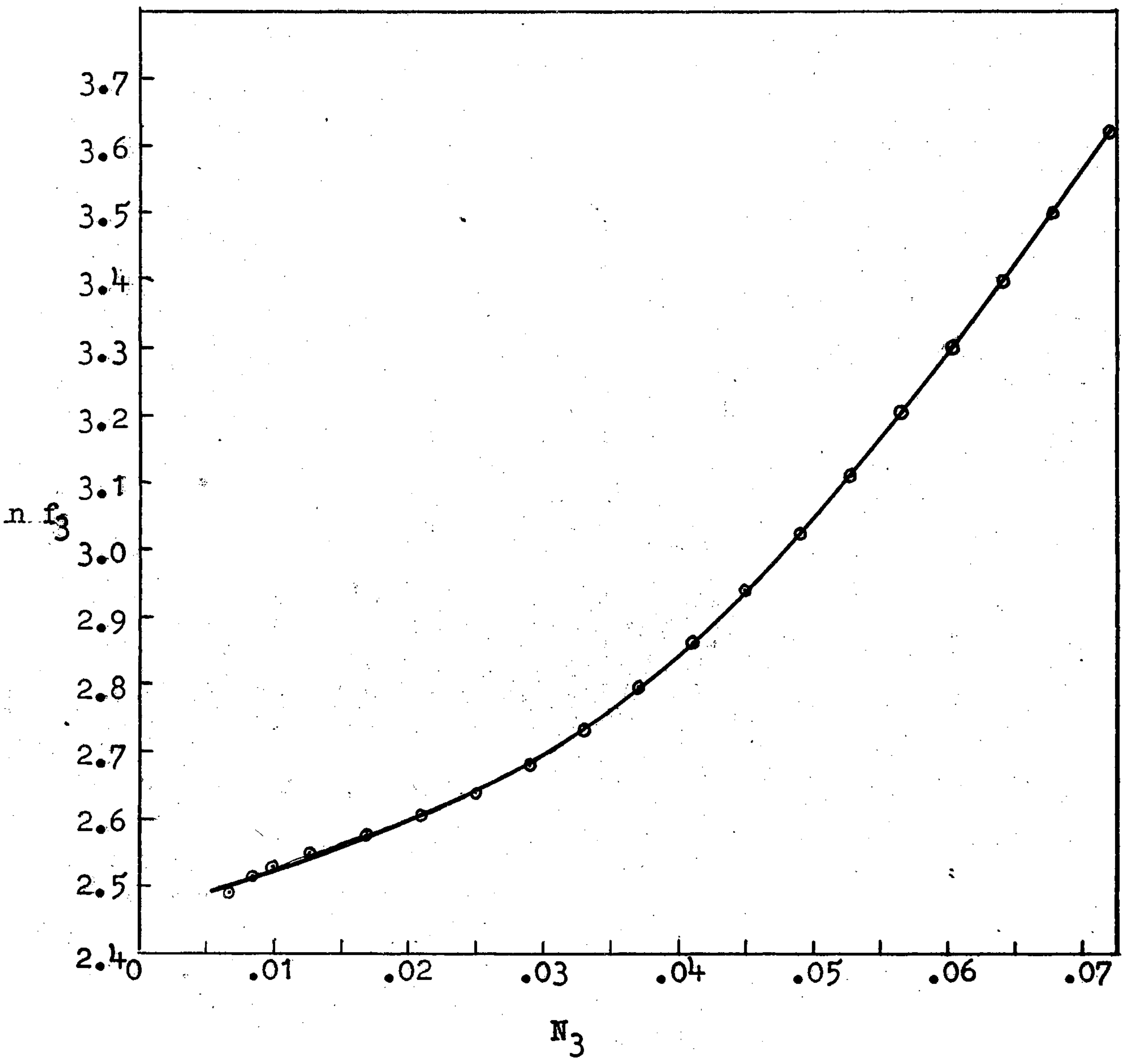
Scatchard in the methanol-carbon tetrachloride system. Addition of carbon tetrachloride to methanol caused the disruption of small strongly bound methanol aggregates and the formation of larger more loosely bound aggregates of methanol and carbon tetrachloride.

Figure 26 shows the activity coefficient of $CoCl_2$ on a mole fraction scale plotted against the concentration (mole fraction) of the salt. The activity coefficient is again computed relative to the saturated binary solution of $CoCl_2$ in methanol taken as unity. Comparison of the curves in Figures 23 and 26 shows that whereas both activity coefficient curves increase with increasing salt concentration, the ternary system does not show the falling off at low concentrations found in the binary system. This is believed to be the result of dissociation in the binary mixtures at lower concentrations. The lowering of the dielectric constant of methanol ($\epsilon = 33.1$) by ethylene chloride ($\epsilon = 10.4$) would be expected to favor ionic associations at greater dilutions than in the binary methanol solutions.

Robinson and Stokes (59) have pointed out that a test of their hydration hypothesis would be a study of ternary systems composed of water, an electrolyte and a nonelectrolyte component which did not solvate the electrolyte. They recognized the difficulty in finding a suitable system for making such a test because of the effect of a change in dielectric constant upon the degree of ionic association. Their equation would attribute all of the deviations from ideality to electrostatic forces and to ionic solvation. An attempt was made to apply similar considerations to the system studied in this research by assuming complete ionic association of cobalt chloride in the binary solvent and no solvation of the $CoCl_2$ by ethylene chloride. Hence all deviations

Figure 26

ln f_3 (Rational Activity Coefficient) of $CoCl_2$ vs Mole Fraction of $CoCl_2$ in the Ternary System MeOH - $EtCl_2$ - $CoCl_2$



from ideal behavior were attributed to solvation. It was found, however, that the Robinson and Stokes theory could not account for all deviations from ideality in terms of methanol solvation alone.

If the above assumptions are made, the Robinson and Stokes theory leads to an equation of the form

$$\log \gamma_3 = - s \log a_1 - \log (x/x^*) \qquad (95)$$

where

γ_3 = activity coefficient of $CoCl_2$ on the mole fraction scale

s = solvation number of $CoCl_2$ with methanol

a_1 = methanol activity

(x/x^*) = ratio of mole fractions calculated without and with consideration of solvation of $CoCl_2$ with s moles of methanol respectively.

Since the ratio of mole fractions is $(n+m_3-s/n+m_3)$ it is obvious that when n (the number of moles of solvent mixture) is constant, and large in comparison with the salt molality m_3, the mole fraction ratio becomes approximately constant and is given approximately by (1 - s / n). In order to test the applicability of Equation (95) to the MeOH - $EtCl_2$ - $CoCl_2$ system, the activity coefficient of $CoCl_2$ must be referred to the state of infinite dilution in the methanol-ethylene chloride solvent mixture. Unfortunately the experimental data do not allow a reliable extrapolation to be made to this state, and as pointed out earlier, the activity coefficients are all referred to the saturated binary mixture of $CoCl_2$ and methanol. Equation (95) becomes, therefore,

$$\log \gamma_3' = - s \log a_1 - \log (1 - s/N) - \log k \qquad (96)$$

where k is the proportionality constant required when the activity coefficients are calculated relative to the state of the saturated solution as mentioned above. The experimental data plotted as log γ'_3 against log a_1 fall on a straight line above about 1.5 molal with a slope of s = 5.3. The data deviate markedly from linearity below 1.5 molal, however. It is doubtful if any great significance can be attached to the linear section, however, because linearity in itself does not constitute a check of Equation (96) since the approximate theoretical value of the intercept log k (1 - s/N), contains the unknown constant k. A plot of Equation (96) is given in Figure 27.

Factors possibly contributing to the nonideality of $CoCl_2$ in the ternary system, other than solvation, might include large differences in molar volumes, configurational entropy, etc. It seems unlikely, however, that such factors are as important as solvation in causing the activity coefficient to increase with increasing concentration. In retrospect it seems probable that a choice of a better understood solvent pair, e.g., MeOH - CCl_4, might have enabled one to give a more satisfactory theoretical interpretation of the experimental data. However, the choice of the methanol-ethylene chloride system was made because it seemed particularly amenable to investigation by the infrared technique, which was one of the primary objectives of this work.

Figure 27

Test of Robinson and Stokes' Hydration Theory

For Ternary Solutions (Modified)

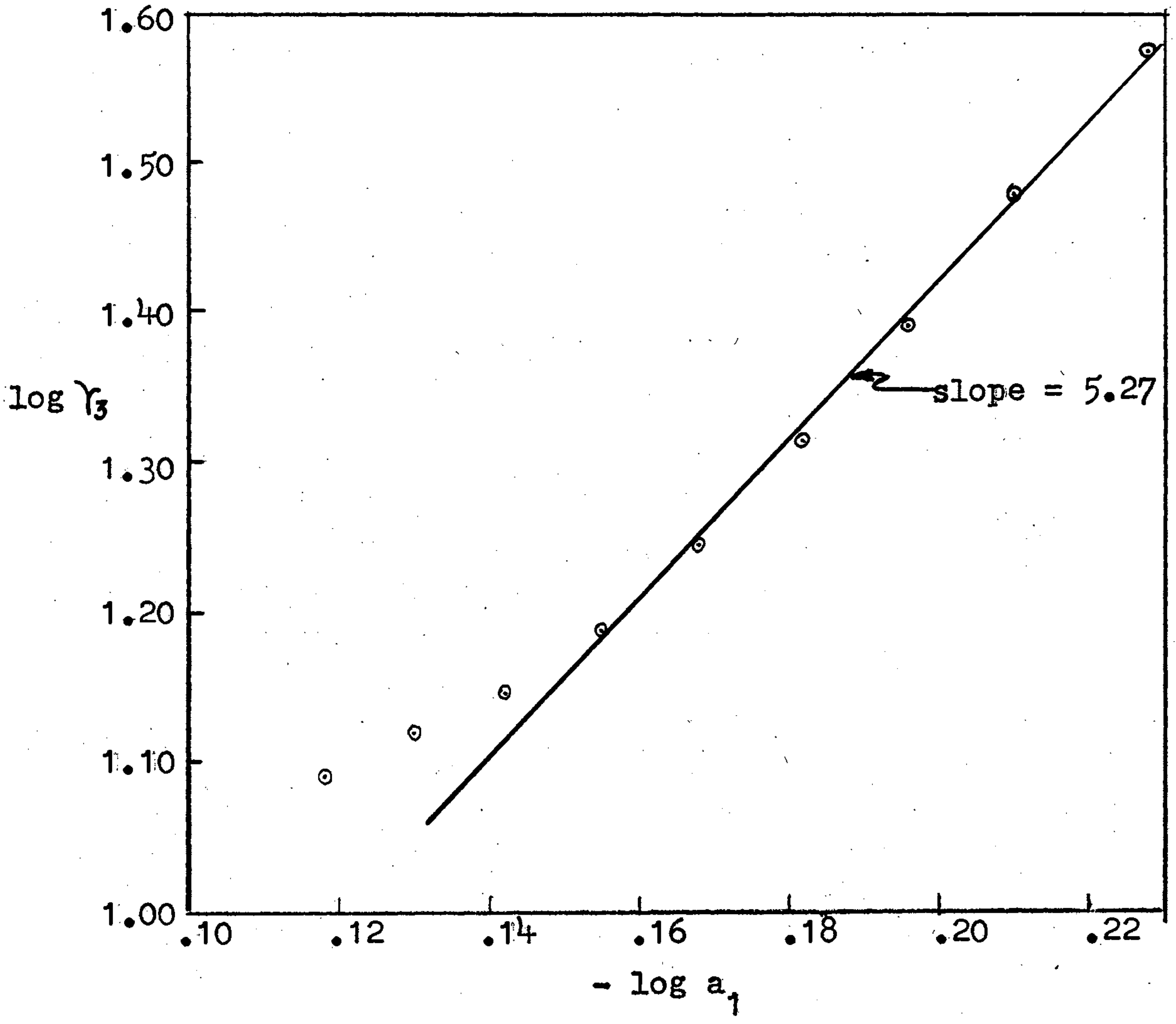
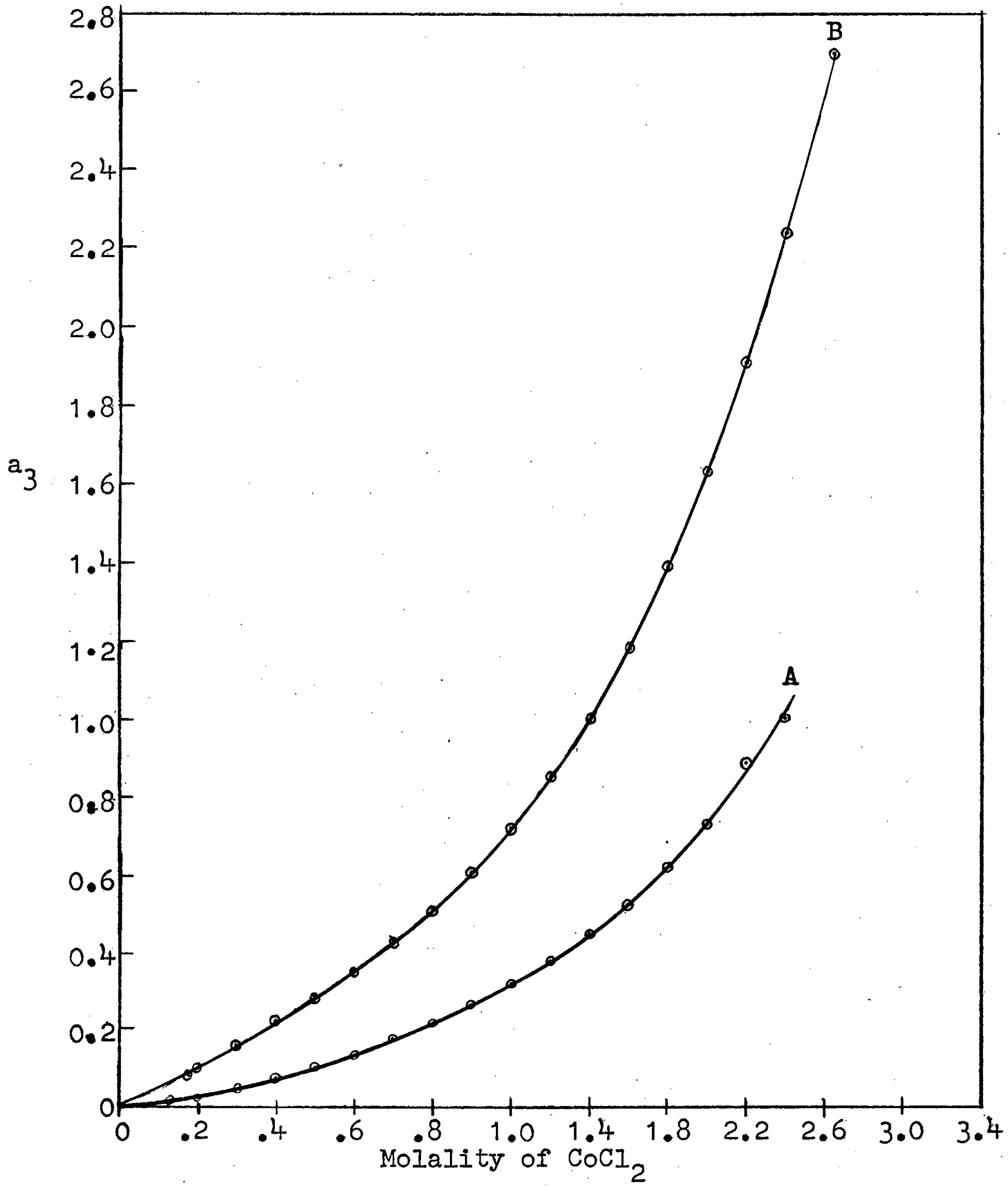


Figure 28

Activity of $CoCl_2$ vs Molality of $CoCl_2$

A Binary System MeOH - $CoCl_2$

B Ternary System MeOH - $CoCl_2$ - $EtCl_2$



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